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Analysis of Hexavalent Chromium in South Carolina Industries

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ANALYSIS OF HEXAVALENT CHROMIUM IN SOUTH CAROLINA INDUSTRIES

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ABSTRACT

Hexavalent chromium is a commonly used industrial anti-corrosive that is carcinogenic and toxic to humans and the environment. Although there have been several studies published over the past two decades on the adverse effects of inhaling and ingesting Cr (VI), it is still readily used and emitted by various industries. This project set out to: 1) identify and analyze a possible pathway to significantly reduce the use and pollution of hexavalent chromium in South Carolina and 2) provide a risk assessment of specific emission sites in the Charleston metropolitan area. The first section of this study examined source reduction of chromium emissions, while a site risk assessment was conducted in the second section. Source reduction involved conducting a cradle-to-grave Life Cycle Assessment (LCA) comparison of hexavalent chromium and titanate, a titanium-based alternative to chromium in metal manufacturing. The risk assessment studied emissions from specific release sites and provided significant data on the environmental and human health impacts of Cr (VI) emissions. The LCA findings bore favorable results for the titanate alternative, while the risk assessment showed significant cause for concern regarding contamination of fish and drinking water within the study area.

DEDICATION

This work is dedicated to my home state of West Virginia and all her wonderful people who are often neglected, especially in the areas of environmental health and safety. We are a consistently overlooked but profoundly resilient and caring people. Our country was built on the backs of our forefathers and mothers working long hours in dark mines and dusty mills to provide power for America. Today we are left picking up the pieces of lost industry and remediating what land is left. Growing up in a state that contained both immense beauty and natural destruction inspired me to be where I am today. Maybe one day my work can help bring my fellow West Virginians and many others hope for the future. Take me Home, Country Roads.

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CHAPTER ONE

I. INTRODUCTION

1.1 Goal/Motivation

The goal of this research is to reduce the use and pollution of hexavalent chromium within South Carolina industries by identifying opportunities for source reduction and assessing the human health risk of current emissions. Hexavalent chromium, also known as chromium-6 or Cr (VI), is a commonly used chemical in various industries (NIH, 2020). Cr (VI) is often used to coat metals, woods, and textiles to prevent corrosion. It is also used in paint/colorant manufacturing and is an emission from coal-burning power plants. The motivation behind this project was the concerning statistics on hexavalent chromium and its links to various health problems including digestive, respiratory, and integumentary system damage (NIEHS, 2020) (NTP, 2008). Similarly, hexavalent chromium can cause cancer in humans and wildlife (Aslam & Yousafzai, 2017) (IRIS, 2010).

This research focuses on source reduction of chromium pollution and risk assessment of current major pollution sites. Source reduction centers on preventing pollution before it happens by redesigning a system and/or switching to alternative chemicals and processes (EPA, Sustainable Materials Methods, 2019). Risk assessment involves studying emissions data and calculating accurate concentration, dose, and risk values for that release to better understand the impact on the environment and human health (Fjeld, Eisenberg, & Compton, 2007).

1.2 Scope

This study focuses on industries within the State of South Carolina. To better understand chromium pollution within the state, Toxic Release Inventory (TRI) data from the EPA was used (TRI, 2019). Moreover, the recent research of Ted Langlois on TRI data mapping aided significantly in this research (Langlois, 2018). The audience for this project is people within the state of South Carolina; however, the report hopes to provide results that can be useful throughout the United States. Specifically, this project is directed toward industries that currently use hexavalent chromium, United States regulatory bodies such as the SC Department of Health and Environmental Control (DHEC), EPA, and citizens of South Carolina that may be unknowingly affected by this pollution.

This study is broken up into two main areas as discussed in the abstract: source reduction and risk assessment. The source reduction section III focuses on finding a viable alternative to chromium use in the metals manufacturing processes and involves a Life Cycle Assessment (LCA) comparing hexavalent chromium to the chosen alternative titanate (EPA, LCA: Principles and Practices, 2006). The risk assessment section IV focuses on two sites, Nucor Steel and BP Chemical in Berkley, SC, that are responsible for the largest direct emissions of Cr (VI) to surface water within South Carolina. At these sites Cr (VI) is dumped directly into surface water; thus, a transport and risk assessment of the releases is conducted to better understand the impacts of the emissions at these sites (TRI, 2019).

CHAPTER TWO

II. BACKGROUND

For over 100 years chromium compounds have been heavily used because of their anti-corrosive capabilities (NIEHS, 2020). This characteristic has made chromium a favorite for use in metal, wood, and other manufacturing industries. The most commonly used industrial version of chromium is in its hexavalent form which yields many environmental problems (NASA, 2020). Over the past decade global governments have started to focus on the negative impacts of hexavalent chromium use, and implementation of regulations banning the chemical in industry has begun (Reisch, 2017).

The most extensive regulations have been set by the European Union (EU). The EU has determined that the use of Cr (VI) in plating solutions for metal manufacturers (largely in aerospace and medical device products) and in paint products will be eliminated within the next decade (REACH, 2019). While this ban was set to start in 2017, the EU has allowed an extension of 7 years for approved companies to experiment with alternatives. In the U.S. there have been no federal bans restricting hexavalent chromium production and use; however, regulations on human exposure from the EPA and OSHA have been implemented to curtail industrial emissions (NASA, 2020). As these regulations increase internationally, the need for chemical alternatives has become a major focus in various industries.

Hexavalent chromium is uniquely dangerous because it has the capability to be harmful both deterministically and stochastically (Fjeld, Eisenberg, & Compton, 2007).

Deterministic risks directly correlate to dose. For example, the severity of acid burn increases as the concentration of hydrochloric acid increases. Stochastic risks are when the probability of harm increases as dose increases. For example, the probability of cancer increases as a person is exposed to increasing levels of benzene. Hexavalent chromium can harm humans via both pathways. Deterministically, Cr (VI) has corrosive and irritant effects to the airway, skin, mucous membranes, and gastrointestinal (GI) tract (NIH, Toxicology Data Network). Stochastically, studies have shown a dose-response relationship between pulmonary cancer and occupational exposure to hexavalent chromium. Moreover, lung, nasal, pharyngeal, and gastrointestinal carcinomas and cancers have been reported to correlate directly with exposure. Lung carcinomas in particular are shown to be higher in individuals regularly exposed to chromates. (Fjeld, Eisenberg, & Compton, 2007)

The cancer-causing ability of Cr (VI) is largely linked to its role as an excellent oxidizing agent. This leads to significant oxidative DNA damage in cells. The 1990s lawsuit and movie based on the life of environmental activist Erin Brockovich brought attention to this problem (Marshall, 1996). Until that point the adverse effects of hexavalent chromium were largely unknown. Ever since, science and engineering have sought out efficient alternatives to chromium use in industry. (NIH, 2020)

2.1 Chemical and Biological Properties

Chromium is a metallic transition element that is the 21st most abundant element on Earth (USGS, Mineral Resources Program, 2019). It is not normally found as an isolated element in nature, but in chromite ores commonly in the form of $FeCr_2O_4$ or $MgCr_2O_4$ (King, 2020). In these ores and throughout nature chromium is mostly found in its trivalent state (CR (III)). Chromium has oxidation states that range from -II (-2) to +VI (6+); however, the most stable forms are trivalent and hexavalent (Cr (VI)) (ATSDR, 2011) (NCBI, 2020). Hexavalent chromium is only found naturally in the rare mineral $PbCrO_4$.

In the scientific community, trivalent chromium is thought to be mostly harmless, if not beneficial (ATSDR, 2011). It is a trace element in various living organisms including the human body. Cr (III) is commonly found in soil, water, and food sources. The Agency for Toxic Substances and Disease Registry (ATSDR), within the U.S. Department of Health and Human Services, discusses trivalent chromium's key role in the insulin production process in humans on their chromium information page (ATSDR, 2011). Moreover, trivalent chromium is essential in the potentiation of insulin and metabolism of glucose. Some dietary supplements contain trivalent chromium because of its theorized propensity to work as an anti-diabetic. Trivalent chromium is usually insoluble and immobile because of how it tends to combine with hydroxides to form stable compounds and precipitates (NCBI, 2020). However, if Cr (III) does get inside an organism it is likely to bioaccumulate over time due to its immobility and insolubility (Bakshi & Panigrahi, 2018).

Conversely, hexavalent chromium is toxic and carcinogenic to many organisms (IRIS, 2010) (NIH, Toxicology Data Network, 2020). Cr (VI) is not found in nature as an independent cation, rather it is typically present as any oxyanion compound such as CrO_4^{-2}. Hexavalent chromium has the unique ability to pass through cell membranes via oxyanion (specifically, sulfate) transport (Samyn & Perrson, 2016). When hexavalent chromium enters the body, it is typically in the oxyanion form of chromate (CrO_4^{-2}) or dichromate ($Cr_2O_7^{-2}$). Both carry a (-2) charge, which is one of the key characteristics that allows hexavalent chromium to be significantly damaging to cells and DNA (Tollefsbol, 2011). Sulfates (SO_4^{-2}) have a (-2) oxidation state and are regularly transported inside of cells to provide required macro-nutrients. This process often happens against a concentration gradient to maintain cell equilibrium. Due to their similar charge, sulfate transporter proteins can confuse chromate species for a sulfate compound and transport harmful hexavalent chromium compounds into the cell. This ability to cross the cell membrane barrier is unique to chromium in its hexavalent state which is why trivalent chromium is not a concern for toxicity and carcinogenicity. In the environment hexavalent chromium is not only soluble but also extremely mobile as well. These attributes coupled with its toxicity and carcinogenicity make for an extremely dangerous pollutant (NIH, 2020).

Hexavalent chromium is a strong oxidizing agent in nature and so too in the human body. In most environments Cr (VI) has an affinity to be reduced and often this reduction occurs in the presence of organic matter such as through reactions within a cell (Tollefsbol, 2011). Once hexavalent chromium enters the cell it is reduced by various

electron containing compounds that are strong reducing agents. Organic matter is largely composed of electron donors such as NADPH that can donate electrons to metals. Carbon is also often in a reduced state in organic matter and has the ability to give up several electrons making it a favorable reducing agent. Because of these biological processes hexavalent chromium is readily reduced to lower valency states and eventually to trivalent chromium in the presence of organic matter.

This reduction of Cr (VI) causes oxidative stress on proteins, lipids, and DNA in cells. Oxidative stress occurs when too many oxygen free radicals are created in a cell and defense mechanisms like antioxidants and enzymes that eliminate oxygen free radicals can't keep the cell in homeostasis (Gagne, 2014). These adverse effects on the cell can lead to cytotoxicity (toxic to cell), genotoxicity (damage to cell's genetic information), and even carcinogenicity (mutations from genotoxicity leading to cancer). This directly describes hexavalent chromium's ability to be both toxic and carcinogenic to humans.

Finally, several studies show that heavy metals like chromium can bioaccumulate in various organisms from inhalation, drinking water, and mainly food exposure (ATSDR, 2008) (Bakshi & Panigrahi, 2018) (RAIS, 2019). Fish and other aquatic life are commonly at highest risk for bioaccumulation because they can easily be surrounded by contamination in water where metals are more concentration than in air. Often, heavy metals accumulate largely in gills, liver, and kidneys of fish (Yousafzai et al, 2017). Gills are directly exposed as fish swim through contaminated areas and digestive organs are affected by ingestion of contaminated food and water. The EPA's

Risk Assessment Information System (RAIS) studies show chromium bioaccumulates significantly in fish which makes it especially aquatically toxic in freshwater and marine environments (Fjeld, Eisenberg, & Compton, 2007) (RAIS, 2019). Commonly chromium enters organisms in the hexavalent form due to its solubility and mobility. Following this exposure, chromium can accumulate in various oxidation states in the body (Bakshi & Panigrahi, 2018).

Chromium normally accumulates in aquatic organisms chronically over time (Aslam & Yousafzai, 2017). This does not lead to an instant kill off but rather a slow build up in the fish tissue until various effects like decrease in fertility, lack of anti-body production, DNA damage, or development of anemia can occur. This contamination is significant when occurring in popular fishing areas where consumption of fish would be common. In this way, chromium's ability to bioaccumulate leads to yet another possible pathway for human exposure.

2.2 Source Reduction of Chromium Pollution

In 1990 the United States created the Pollution Prevention Act (PPA) to increase industry interest in source reduction instead of treatment and disposal of various pollutants (EPA, Sustainable Materials Methods, 2019). With this law, the goal was to focus on reducing waste produced by optimizing industrial processes and finding alternative raw materials. However, many industries currently focus on end-of-life solutions like treatment and disposal rather than source reduction because they can still meet environmental compliance regulations. This mindset can be detrimental to humans

and the environment because contaminants like hexavalent chromium are very hard to treat and remediate once they are released to the environment. A push toward finding chemical alternatives for hexavalent chromium in various industrial processes is necessary to secure a safer environmental future.

The EPA uses an inverted triangle called the Waste Management Hierarchy to describe most preferable to least preferable methods of reducing waste and pollution as shown in Figure II-1. As seen below source reduction is the most preferred method of waste reduction. (EPA, Sustainable Materials Methods, 2019)

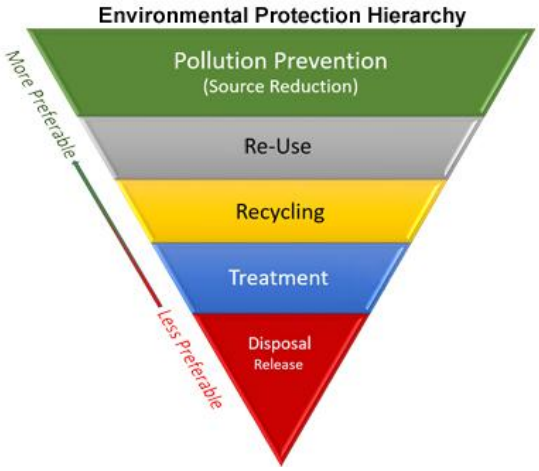


Figure II-1: Waste Managemen Hierachy

Environmentally Preferable methods of waste management (EPA, 2019)

As discussed, hexavalent chromium pollution comes from various industrial processes. Thus, focusing on discovering alternatives to hexavalent chromium can be difficult because it is produced and used for several different reasons. For example,

primary metal manufacturing (#1 Cr (VI) pollution producer), electricity generation (#2) and fabricated metal manufacturing (#3) are major producers of hexavalent chromium pollution in South Carolina (TRI, 2019). Primary metal production involves the creation of metal alloys like steel or aluminum that eventually get sent off for several uses. Fabricated metal includes products that take the primary metals and create something usable such as a car or refrigerator. Together primary and fabricated metal manufacturing make up roughly 67% of total chromium pollution within South Carolina over the last 5 years of TRI data (2011-2016). Cr (VI) is used to provide an anti-corrosive layer to various metals that would otherwise corrode in the environment which leads to heavy use in both primary and fabricated metals manufacturing. As chromium solutions are used in metal processes they can be released in air, water and soil (Williams, 2011). Cr (VI) air emissions can occur as many metal processes require high heat and therefore have evaporation of contaminants. Soil and water emissions occur as excess solution is sent to holding areas for treatment and disposal or directly released into the environment. The distribution of hexavalent chromium pollution in South Carolina by industry can be seen in Figure II-2.

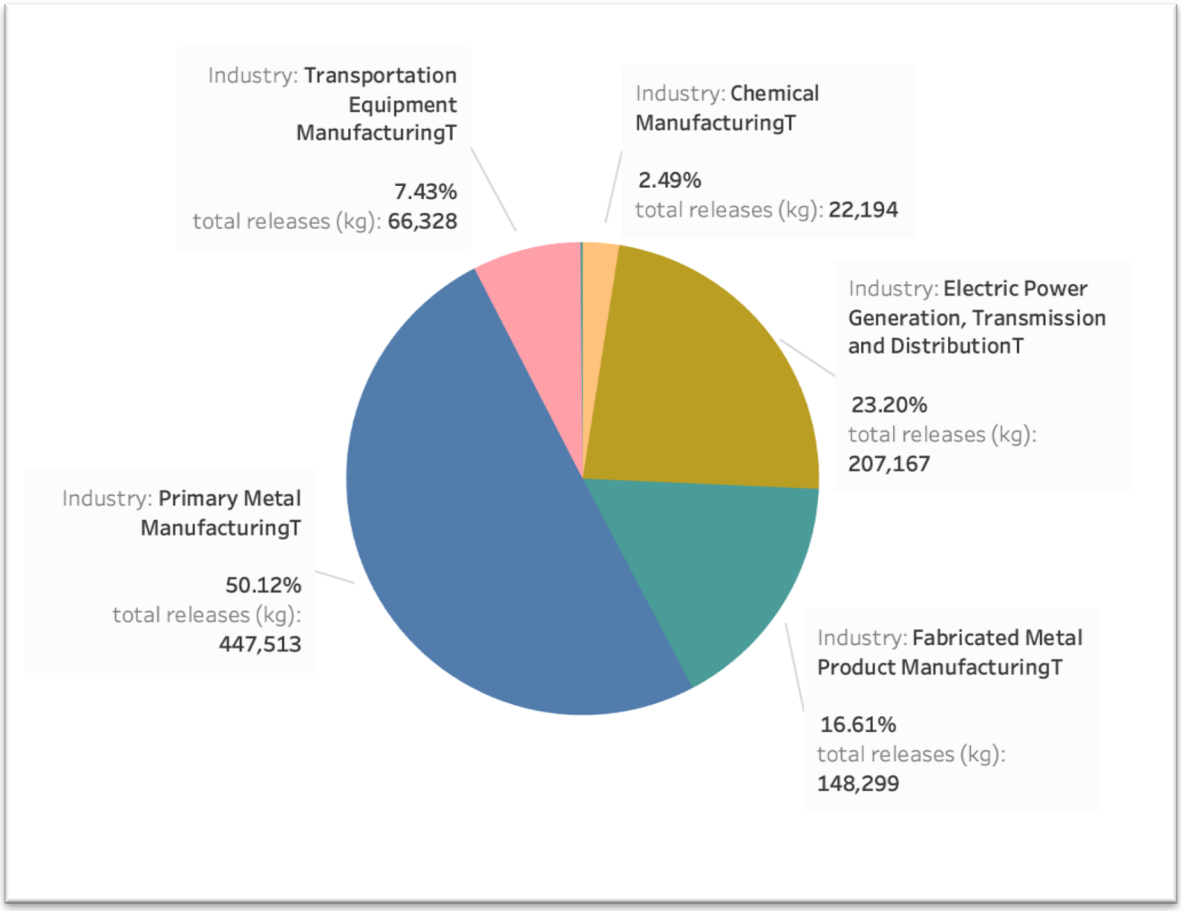


Figure II-2: Distribution of Chromium Releases by Industry in South Carolina over the last five years of TRI data (2011-2016) (EPA, 2019)

Meanwhile, electric power production is the second largest producer of hexavalent chromium pollution largely because of the chromium content within burned coal (Kravchenko, 2018). As this coal is burned for electric power plant production, significant amounts of hexavalent chromium are released to the atmosphere. Moreover, unusable coal ash is mixed with water and sent to storage ponds where coal is meant to be kept indefinitely. These slurry ponds often leak contaminants into groundwater and

surface water (ATSDR, 2008). This provides an easy way for hexavalent chromium to spread in the environment in air, ground, and water.

Finding a method of source reduction is difficult when looking at electric power plants. This process would require a removal of chromium from coal before coal burning which would be extremely energy intensive, inefficient, and likely impossible (Kravchenko, 2018). Fortunately, data shows a steady decrease in electric power-based chromium pollution over the last ten years of data studied as seen in Figure II-3. This is most likely due to South Carolina's energy sector (and the U.S. as a whole) moving away from coal to gas or nuclear as electric power plant fuel (EIA, 2018). Conversely, a steady increase in metal manufacturing pollution is also observed in the same figure.

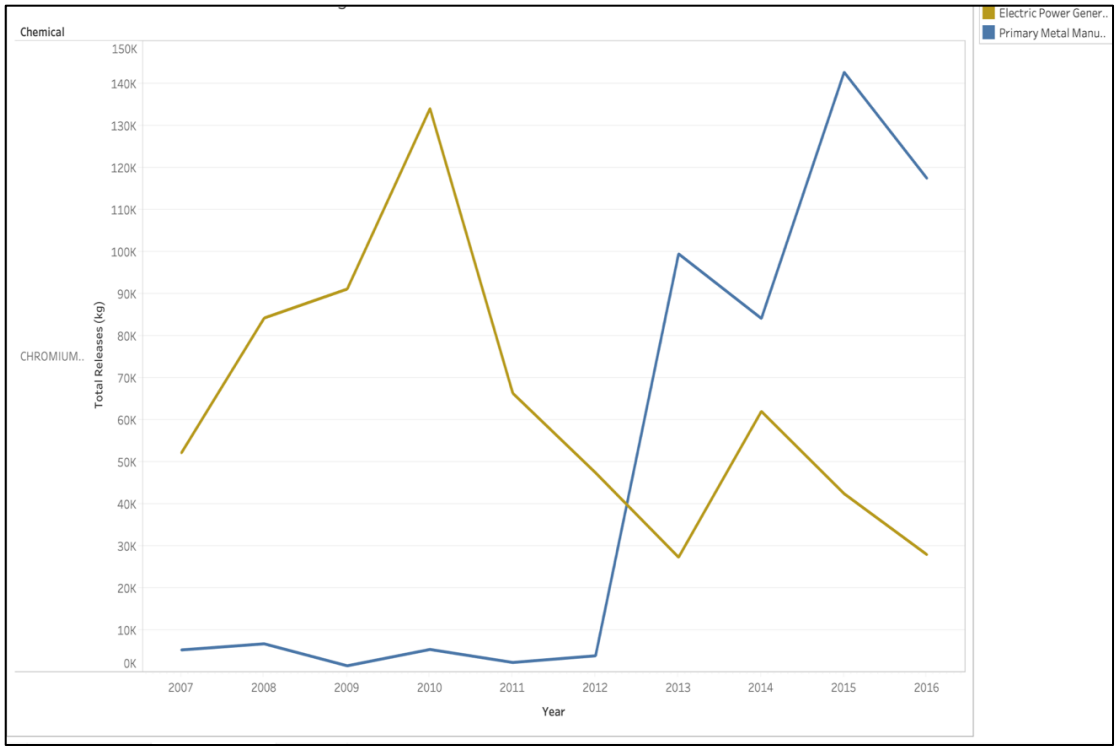


Figure II-3: 10-year trend of total Chromium Releases

from electric power generation (yellow) and primary metal manufacturing (blue) (EPA, 2019)

With this data in mind, it was decided to focus on metals manufacturing as the industry in which source reduction is more plausible and could yield immediate benefits. Eliminating hexavalent chromium from metals manufacturing would have a significant impact on overall releases (67%) and would provide an initial avenue for industries to make a difference (TRI, 2019).

2.3 Seeking an Alternative

Chromium is an exceptional anti-corrosive with unique properties and chemistry that allows it to perform well. In metal manufacturing chromium usually is

used to create a passive oxide layer (passivation) on the metal of choice that protects the corrosion-prone metal (Williams, 2011). Passivation is the process of using a metal oxide such as chromium to build a shield around the prone metal. The chromium oxide then protects the metal from oxidation and reduction due to outside elements. (LibreTexts, 2019)

Due to this exceptional metal oxide ability, hexavalent chromium was used for over a century around the world with few limitations. Since the health scare of Cr (VI) arrived in the 1990s, some research has focused on finding viable replacements for hexavalent chromium in industry in order to eliminate it altogether (Harscoet & Froelich, 2007). However, hexavalent chromium's ability to outperform several similar anti-corrosive agents has made it difficult to find an alternative chemical compound (Williams, 2011). A chemical that can both perform at the same level as chromium and also be significantly better for humans and the environment has been hard to find.

One idea that has provided some success in the past two decades is the switch to trivalent chromium-based plating because of the lower environmental impacts (Protsenko & Danilov, 2014). Cr (III) coatings have been created and used in the metal plating industry (EPI, 2020). However, the use of trivalent chromium still releases chromium to the environment which could become oxidized into Cr (VI) (Williams, 2011). Moreover, Cr (III) has the tendency to complex into several different compounds which can lead to impurities in the metal oxide coatings. Due to these inadequacies it is vital to find a reliable and safe alternative to Cr (VI) oxide coatings for the future of industry.

2.3.1 Titanate

Over the past decade, interest in finding alternatives to chromium-based oxide coatings for both ferrous and non-ferrous metals has increased steadily as regulations regarding hexavalent chromium use become more stringent (REACH, 2019). This has led scientists and engineers around the world to research the use of alternative metal oxides that would be less threatening to humans and the environment. A metal that has been of interest recently is titanium. Titanate is a name used for variations of anions that contain both titanium and oxygen. At the start of this project, a study regarding titanate as an alternative was found in a published master's thesis by Melissa Williams at the University of Rhode Island (Williams, 2011). Williams' research focused on finding an alternative anticorrosive to chromates for use specifically for aluminum corrosion protection. The study described the need for extra corrosion protection on aluminum in certain environments.

Aluminum was also chosen to be the substrate studied for the research conducted herein. The continuing transition from heavier steel-based machines toward lighter weight aluminum parts in industry has made aluminum a crucial metal of the present and future. In recent years federal regulations on emissions standards have forced industries such as car manufacturers to move toward a higher aluminum to steel ratio in their designs (GRV, 2019). The goal was to significantly cut down on vehicle-born emissions by decreasing the weight of the car parts. The EPA estimated that the transition to aluminum for some designated models from 2012-2025 will save up to 6 billion tons of CO_2 emissions over the vehicle lifetime (Burnett, 2014).. Moreover, aluminum is readily

used in aerospace and the demand for it continues to increase as both government entities and private organizations strive for further space exploration (Rambabu, Prasad, Kutumbarao, & Wanhill, 2017). Therefore, a continuous stable increase in aluminum production and use is predicted in the next decade (GRV, 2019) As the U.S. increases its dependency on aluminum, it is vital that the chemicals used with aluminum are environmentally responsible.

It is important note that aluminum does have a natural oxide layer that provides some protection for the substrate. However, in environments where high concentrations of salts (marine) or consistent exposure to weathering (cars/aerospace) can cause excessive damage to aluminum, a separate oxide layer is required (Williams, 2011). This extra layer of protection has historically come from hexavalent chromium-based oxides. Yet, Williams' report showed that the anion titanate could perform just as efficiently as hexavalent chromium in a lab-scale setting and suggested it would most likely be at a much lower environmental impact.

In recent years several other studies have similarly looked at titanium-based oxide (titanate) coatings in lab studies (Milosev & Frankel, 2018) (Xiao, Tang, Fan, Xiao, & Wang, 2017) (Zhan, et al., 2019). Conclusions from these reports point to titanium's exceptional performance on both ferrous and non-ferrous metal substrates. Furthermore, these studies have shown the excellent ability of titanium-based oxide coatings not only for aluminum substrates, but steel as well. Most importantly, they also point to titanium's compatibility with biological systems and low impact on organism health.

Chemically, titanium and chromium are very similar in their aqueous state which allows them to have similar anti-corrosive abilities (Williams, 2011). More specifically, titanium and chromium show similar attributes on their respective Pourbaix diagrams including similar oxidation states and chemical passivity zones. Pourbaix diagrams show electronegativity of aqueous environment (pE) vs. pH of the aqueous environment (LibreTexts, 2019). Readers are referred to Marcel Pourbaix's "Atlas of Electrochemical Equilibria in Aqueous Solutions" pages 72-73 and pages 262-263 for titanium and chromium's respective Pourbaix diagrams (Pourbaix, 1966). Together the pE and pH properties display how a chemical will speciate in different environmental conditions. The similarities between the two chemicals also directly relate to titanium's excellent ability to act as an anti-corrosive coating in place of chromium. Pourbaix diagrams for titanium show a much larger passivity range than chromium, thus the argument could be made for titanium being an even better anti-corrosive than chromium.

2.3.2 Titanium: History and Background

Titanium is largely popular because of its aforementioned anticorrosive ability and its incredible strength. These attributes have led to its prominent role in manufacturing and construction since the early to mid-1900s. In the 1940s, the Becher process was created and revolutionized the titanium industry (Figure II-4). The process allowed manufacturers to produce clean high-grade titanium compounds called rutile from lesser compounds called ilmenite (Zhang, Zhu, & YongCheng, 2011). With this process allowing for easier and cheaper extraction of higher quality titanium, use has

grown in the world over the past 75 years. Titanium is the 9th most abundant element on earth which allows for a significant amount of resources (Kyocera, 2019). It is an attractive element because of its amazing strength and low environmental impacts compared to Cr (VI) (Lab, 2018). Studies have shown no known human side effects and few ecotoxicity problems from titanium use. Titanium today is commonly consumed in food coloring and as a whitening agent in toothpaste (Gázquez, Bolívar, Garcia-Tenorio, & Vaca, 2014).

Although titanium has excellent biocompatibility and high strength, manufacturers may be hesitant to switch from a well-known coating process such as the chromium-based process to a titanium-based process. Studies have shown that hesitation to switch from chromium coatings in metal manufacturing is often due to unfamiliarity with one process and comfortability with another, rather than preference due to actual performance of the coating (McCrea & Palumbo, 2011). Moreover, a fear of implementation cost from overhauling manufacturing processes and making them compatible with a different material may add to the resistance against transitioning. These barriers must be overcome in order to successfully transition away from chromium and toward titanium. An acknowledgement of long-term benefits for employee health, metal performance, and the local environment is necessary to create a shift in the metal manufacturing sector. Similarly, a better understanding of the cost savings from having these healthy employees and fewer environmental fines is also needed (CDC, 2015).

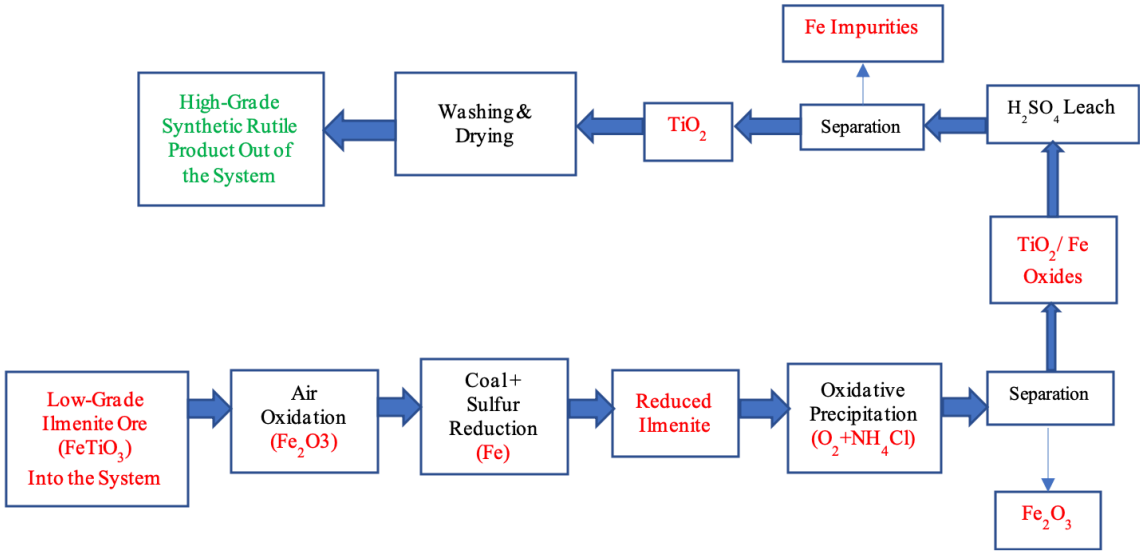


Figure II-4:The Becher Process

Takes in low-grade titanium ore (ilmenite) and produces high-grade synthetic rutile that can be then used for anti-corrosion application

The results from the titanium coating studies previously discussed led to the conclusion that titanate had the anticorrosive ability to be an effective alternative. The most important factor moving forward, and a significant part of this research, was to directly compare hexavalent chromium against titanate in a Life Cycle Assessment.

CHAPTER THREE

III. LIFE CYCLE ASSESSMENT

According to the EPA a life cycle assessment (LCA) is an analysis that compares industrial products, processes, or materials from cradle-to-grave to fully understand environmental and human health impacts (EPA, LCA: Principles and Practices, 2006). Cradle-to-grave refers to a life cycle from raw material extraction to end-of-life disposal, reuse, or recycling. The International Organization for Standardization (ISO) defines LCA as:

"A technique for assessing the environmental aspects and potential impacts associated with a product by: compiling an inventory of relevant inputs and outputs of a product system, evaluating the potential environmental impacts associated with those inputs and outputs, interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study (ISO 14.040)." (Agder, 2019)

Life cycle assessments are more inclusive than a typical environmental assessment and take into account water use, energy use, and transportation, as well as the main system being studied. In this way, LCAs account for various possible impacts of a product system that may otherwise be forgotten. The ultimate goal is to have a comprehensive, dependable, and fair comparison. This is done by compiling accurate energy, raw material, and water inputs as well as inventory of all environmental emissions; evaluating potential impacts from inputs, processes, and releases; and properly interpreting results to provide a clear and concise explanation of impacts. (EPA, 2006)

Life cycle assessments are made up of four main phases according to the ISO: 1) goal and scope definition, 2) inventory analysis, 3) impact assessment, and 4) interpretation. Accurate choices in each of these phases are crucial to conducting a proper Life Cycle Assessment. The EPA describes each of these stages as:

Goal - includes determining what the desired outcome of the assessment may be. It is also important to determine an audience in the goal.

Scope - focuses on describing the product, process, or material. It also includes setting system boundaries that adequately include the variables the researcher intends to study.

Inventory Analysis - is a step where the researcher identifies and quantifies the systems energy, water, and material use and releases to the environment.

Impact Assessment - evaluates the possible environmental and human health effects of said inputs, usage, and releases identified in the inventory analysis.

Interpretation – comprehends the results from the inventory and impact phases in order to yield a preferred product, process, or material. It is important to be aware of uncertainties and assumptions chosen throughout the LCA to be able to clearly relay the results to the desired audience.

These four phases are considered to be iterative as seen in . (EPA, 2006)

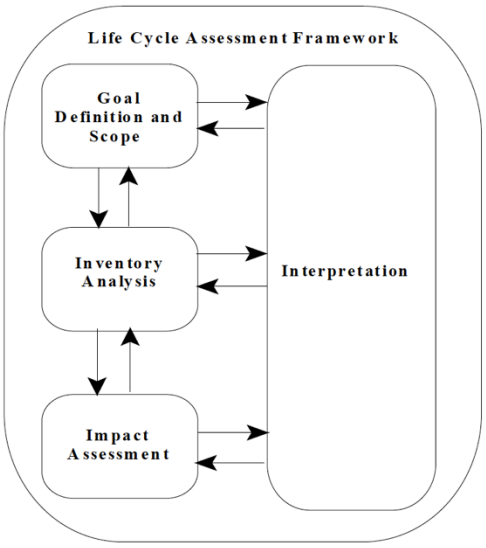


Figure III-1: Interconnecting Phases of LCA

(EPA, LCA: Principles and Practices, 2006)

This Life Cycle Assessment was conducted with openLCA modeling software. openLCA is a completely free and extensive modeling software that was created to provide LCA capabilities to anyone who may be interested. Previously, all modeling software was expensive and intended for use by large corporations. The low cost of openLCA allowed this research to be conducted at minimal expense and provided access to a variety of useful databases. (OpenLCA, 2020)

The database chosen for this study was ecoinvent 3.2. A quality database is especially necessary for the inventory analysis phase where access to accurate industry and energy data is vital to the overall ability of the LCA. Ecoinvent has been providing data for Life Cycle Assessments for decades and includes over 17,000 data sets from several countries, industries, materials, chemicals, and processes. (Ecoinvent, 2020)

3.1 Goal and Scope

3.1.1 LCA Goal

The original goal of this LCA was to find a viable alternative to hexavalent chromium based anti-corrosive oxides to support source reduction efforts. This LCA is mainly directed at state and federal environmental policy makers (DHEC/EPA) and industries that contribute to Cr (VI) emissions. The motivation behind this project was the concerning statistics on hexavalent chromium and its links to cancer in humans and wildlife, and its ecotoxicity. The alternative had to be efficient i.e. perform just as well as chromium, and had to have lower impacts on environmental and human health. Following further investigation of titanium-based coatings, titanate was chosen as a possible alternative. This was largely due to its ability to perform just as well as chromium with decreased environmental impacts (Williams, 2011). While studies on titanium-based coatings were intriguing, no LCA comparing their production and use phases to hexavalent chromium's was found. A clear comparison of energy and environmental impacts is an important step needed in finding a promising alternative.

3.1.2 LCA Scope

The boundary of this LCA was decided to include only the processes, energy, and emissions required from machines and transport to perform each process. Money and energy to manufacture capital equipment was not included; machines and trucks were considered already built. Likewise, this study did not include any human worker needs including food, energy, or water. This would be too expansive for the goal at hand. The

LCA was run as a cradle-to-grave LCA to fully understand all environmental impacts of both processes at every level. A functional unit of 10,000 m^2 of anodized aluminum was chosen. This was chosen largely because it was the functional unit used in a chromium LCA paper that provided significant data for this project (Harscoet & Froelich, 2007). Moreover, the corrosion protection abilities of both chromium and titanium-based processes were assumed to last throughout the life cycles of the products. Thus, the assumption was made that both coatings last through their end of life stage. each product to compete equally.

3.1.3 Assumptions

This study required various assumptions. To start, chromium was assumed to be mined in South Africa as the U.S. has no significant chromium mines. South Africa was chosen because it was surprisingly one of the closest countries to the U.S. of all countries that had significant amounts of chromium deposits (USGS, Estimates of Electricity Requirements for the Recovery of Mineral Commodoties, 2011). A distance of 1,000 km of freight train transport from mine to port city was assumed for South African chromium. This value was calculated from an average of distances from two major chromium mines in South Africa (Dwarsrivier and Nkomati mines) to two major port cities: Durban and Port Elizabeth (ARM, 2008) (PCC, 2020). From South Africa the transport was directed to a chromium manufacturer in Rock Hill, SC. The company was found via a Google search for chromium manufacturers in SC. The distance from a coastal point in South Africa (Port Elizabeth) to Charleston Harbor was found to be

roughly 13,285 km via sea transport. A second transport for freight train was added from Charleston Harbor to Rock Hill at a distance of roughly 300 km. This distance along with all others were found via Google maps. Finally, distance to Clemson from Rock Hill was measured for the use phase which was determined to be 200 km. This transportation was assumed to be by lorry (semi-truck). (GoogleMaps, n.d.)

Meanwhile, titanium was assumed to be mined in Aurelian Springs, North Carolina as titanium is commonly mined there (Titanium in the Old Hickory Mineral Sand Deposit, 2016). The titanium was then assumed to be shipped by freight train to Mt. Pleasant, SC (547 km) where a titanium manufacturing plant is present. Finally, for use phase it was shipped to Clemson by lorry which was a distance of 394 km (GoogleMaps, n.d.). Other assumptions included the type of fuel for electricity production and no recycling. In the US electricity was assumed to be produced mainly by a production mix where natural gas was the main fuel because it is the current leader in electricity production in the U.S. (EIA, 2018). The only process that happened anywhere outside the US was the chromium ore mining and for this process electricity from a South African production mix was used. Finally, energy requirements for electricity and heat (MJ) when mining titanium were assumed to 286% higher than for mining chromium (Nuss & Eckelman, 2014). Moreover, energy required for coating aluminum with each product was assumed to be the same. Finally, no energy, material, or emissions inputs and outputs were included for aluminum production since the same amount of aluminum would be coated for each chemical.

Regarding economic differences, at first it was thought titanium ore would be significantly more expensive than chromium ore. However, after researching global markets it became clear that the low-grade titanium ore (ilmenite) commonly found in the U.S. was similar in pricing to chromium ore (Bulletin, 2019). Thus, it was decided that economic analysis was not a major issue to focus on for this project.

3.2 Inventory Analysis

While preparing for this LCA, an exceptional paper was found regarding an LCA performed by Erwan Harscoet and Daniel Froelich. This paper discussed the life cycle of hexavalent chromium in the aluminum anodizing process. Their LCA was conducted using data collected from studying actual industrial processes at the chromium anodizing facility. The processes, chemicals, and other values contained within Harscoet and Froelich's paper were used for the titanate vs. hexavalent chromium LCA. This allowed for accurate modeling of chromium use within the aluminum anodizing process. (Harscoet & Froelich, 2007)

The flow processes for both products were recreated for the assumptions of this project. Each flow diagram shows the product from cradle to grave.

Figure III-2 displays the simplified process flow for chromium and titanium. Regarding elemental flows, 2,825 kgs of both chromium and titanium ores were chosen as the amount of ore originally mined to be able to eventually coat 10,000 m^2 aluminum (USGS, Estimates of Electricity Requirements for the Recovery of Mineral

Commodoties, 2011). Thus, all future impacts discussed are a direct result from that amount of mined ore. (Harscoet & Froelich, 2007)

Energy and material inputs for each process can be seen in and Figure III-4. In every step of each process electricity and heat were needed at varying amounts for each chemical and specific step. Transportation was required in three out of five steps for chromium and two out of four with titanium. All chemical transformation processes were assumed to happen at one site thus transportation is zero during these steps. In the creation of sodium chromate limestone and sodium carbonate were required while sulfuric acid was required to create sodium dichromate and chromium trioxide. A further addition of sulfuric acid was needed for the coating step along with sodium hydroxide and hydrochloric acid (Harscoet & Froelich, 2007).

In the titanium process the Becher process requires inputs of coal, oxygen, sulfuric acid, and ammonium chloride (Zhang, Zhu, & YongCheng, 2011). The sodium titanate creation step has an input of sodium carbonate, while the coating phase for titanate does not require other chemical inputs in this system.

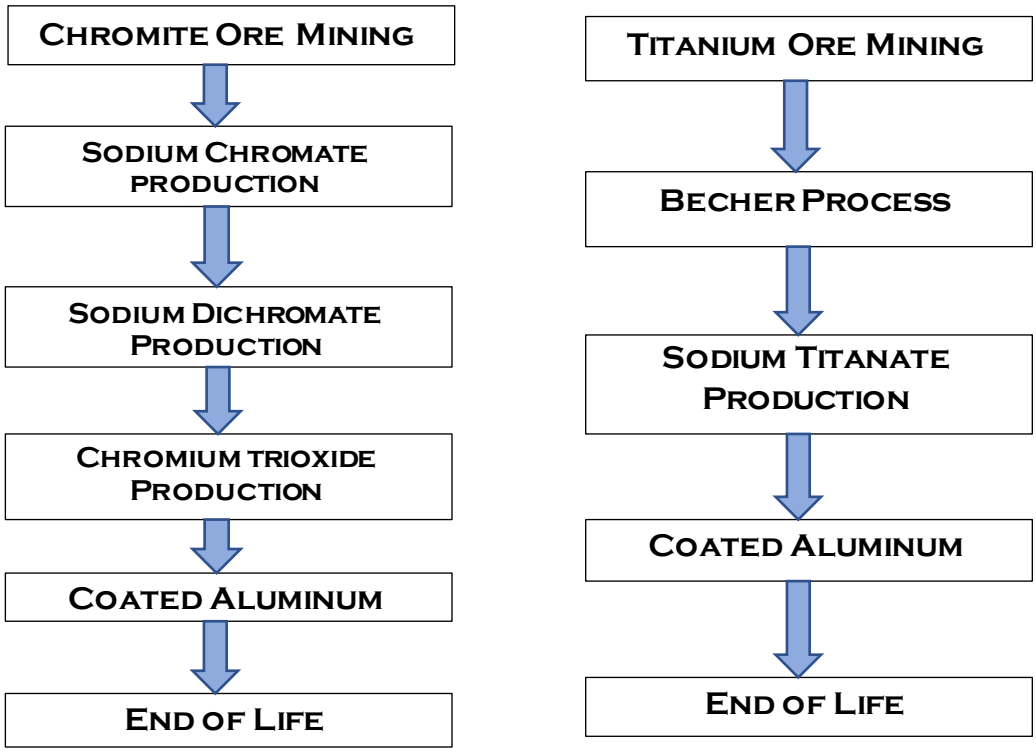


Figure III-2: Process Flows

Chromium from mine to end-of-life on the left (Harscoet & Froelich, 2007)

Titanium from mine to end-of-life on the right (Gázquez, Bolívar, Garcia-Tenorio, & Vaca, 2014) (Stenina, et al., 2016)

Chromium Process Inputs										
	Mass (kg)	Electricity Required (MJ)	Heat Required (MJ)	Water (kg)	Transport Distance (km)	Sodium Carbonate (kg)	Limestone (kg)	Sulfuric Acod (kg)	Sodium Hydroxide (kg)	Hydrochloric Acid (kg)
Ore mining	2825	380	228	7600	1000	0	0	0	0	0
Sodium Chromate	2825	565	21000	0	13285	1957	743	0	0	0
Sodium Dichromate	2616	1144	42000	53	0	0	0	725	0	0
Chromium Trioxide Product	1767	1580	2638	40	0	0	0	1319	0	0
Aluminum Coating	1319	130000	890000	0	250	0	0	108	1005	486

Figure III-3: Energy and materials inputs Chromium Process

Titanium Process Inputs										
	Mass (kg)	Electricity Required (MJ)	Heat Required (MJ)	Water (kg)	Transport Distance (km)	Sodium Carbonate (kg)	Oxygen (kg)	Sulfuric Acid (kg)	Ammonium Chloride (kg)	Coal (kg)
Ore mining	2825	1087	652	7600	504	0	0	0	0	0
Becher Process	2825	591	500	0	0	0	74	441	241	378
Sodium Titanate	1497	100	3	0	0	661	0	0	0	0
Aluminum Coating	1319	130000	890000	0	394	0	0	0	0	0

Figure III-4: Energy and materials inputs Titanium Process

3.3 Impact Assessment

In every Life Cycle Assessment, it is important to choose impact categories to focus on for the desired results of the study. Impacts are split into *Midpoint Impacts* and *Endpoint Impacts*. Midpoint Impact categories account for increases in releases that affect certain environmental areas. For example, an increase in greenhouse gases increases global warming or an increase in the acid content of rain increases acidification. Meanwhile, Endpoint categories focus on how these increases can eventually increase chances of cancer in humans or animals and/ or loss of biodiversity. (EPA, 2006) (Langlois, 2018)

This LCA uses the EPA's Tool for the Reduction and Assessment of Chemicals and other environmental Impacts (TRACI) to determine impacts for the system. Specifically, TRACI version 2.1 was used for this assessment. Impact categories in the TRACI program include ozone depletion, global warming, acidification, eutrophication, photochemical smog, human health cancer, human health non-cancer, ecotoxicity, fossil fuel use, land use, and water use. For this LCA, the most important categories to focus on were decided to be human health cancer and non-cancer, and ecotoxicity. Although these three impact categories were focused on, all TRACI categories were taken into consideration and evaluated (EPA, 2006). Abbreviations used in this report for all impact categories are as follows: smog formation (SF), particulate matter (PM), global warming potential (GWP), ozone depletion (OD), acidification potential (AP), eutrophication (EU), fossil fuel depletion (FFD), human health carcinogenic (HHC), human health non-carcinogenic (HHNC), and ecotoxicity (ECO).

In the TRACI impact program human health cancer and non-cancer are measured by a unit called CTUh. This stands for comparative toxic unit human health and is a measurement of roughly how many people may be harmed per kg of released contaminant. Thus, a CTUh measurement of 5 would mean roughly five people may be affected per kg of contaminant released. For the cancer category this would mean the possibility of five cancer cases, while for the non-cancer category this would mean deterministic harm. To measure ecotoxicity in TRACI 2.1 CTUe is the measurement used. This stands for comparative toxic units of ecotoxicity and is a slightly more complex measurement than CTUh. CTUe is calculated as the potentially affected fraction of species integrated over time and volume per kg of contaminant released (PAF*m^3 *day/kg). It is important to note that both CTUh and CTUe do not yield definitive quantities, but rather probable estimates of human and environmental effects based on a variable range of geographical areas and environmental conditions. Therefore, these values should be look at more as a comparison between the two subjects being studied rather than a definitive amount of harm that will be done to living systems. (Golsteijn, 2014) (Langlois, 2018) (USEtox, 2020)

3.3.1 Results

As hypothesized, the titanate came out as the clear favorite between the two products. It significantly bettered hexavalent chromium in every impact category except global warming where it was slightly higher than chromium. Titanium producing more CO_2 than chromium is supported by literature and thus an expected result (Sanchez-

Segado, Makanyire, Escudero-Castejon, Hara, & Jha, 2015). Titanium's higher CO_2 impact is likely due to the Becher process which uses coal while the chromium process has no step that directly requires coal (Zhang, Zhu, & YongCheng, 2011). Interestingly, titanium has a higher global warming potential but a smaller fossil fuel depletion. The best hypothesis for this phenomenon is again related to the use of coal in the titanium process. Burning coal may give off more CO_2 emissions while the rest of the titanium process is using less fossil fuels than chromium.

Chromium showed an extremely high carcinogenic affinity with 1.92 CTUh as compared to titanium's low CTUh of 2.68×10^{-3} as shown in . Moreover, the carcinogenic data for the titanium process wasn't from the titanium itself, but rather from heat and electricity production. Yet, chromium's carcinogenic data was largely from the metal itself. The 1.92 CTUh for chromium means roughly two people could get cancer per kg of emissions from the chromium used in this process. Similarly, chromium was worse than titanium in the non-carcinogenic human health category at roughly 0.112 CTUh to titanium's 0.0154 as seen in . Again, when looking at the step-by-step breakdown of the two processes, it was clear that most of titanium's non-cancer harm came from stages such as electricity production rather than the product itself. Most of chromium's non-cancer harm came from the product itself.

A better understanding of impacts can be seen by looking at emissions data for each step in the metal processes. The most carcinogenic process for chromium was the chromium trioxide (CrO_3) production process with a direct contribution of .658 CTUh as seen in Figure III-6. A close look at the figure shows that the aluminum anodizing

process in chromium production was a close second for direct contributions to cancer with .635 CTUh, followed by sodium dichromate production at .627 CTUh. Meanwhile, the aluminum anodizing process was the most impactful for non-carcinogenic harm with chromium.

The titanium process showed a majority of impacts coming from the high heat and electricity requirements in the aluminum anodizing step. This step provided 2.61×10^{-3} CTUh of the total 2.68×10^{-3} for carcinogenic harm (Figure III-7). Similarly, it was responsible for 0.0151 CTUh of the total 0.0154 CTUh for non-carcinogenic harm.

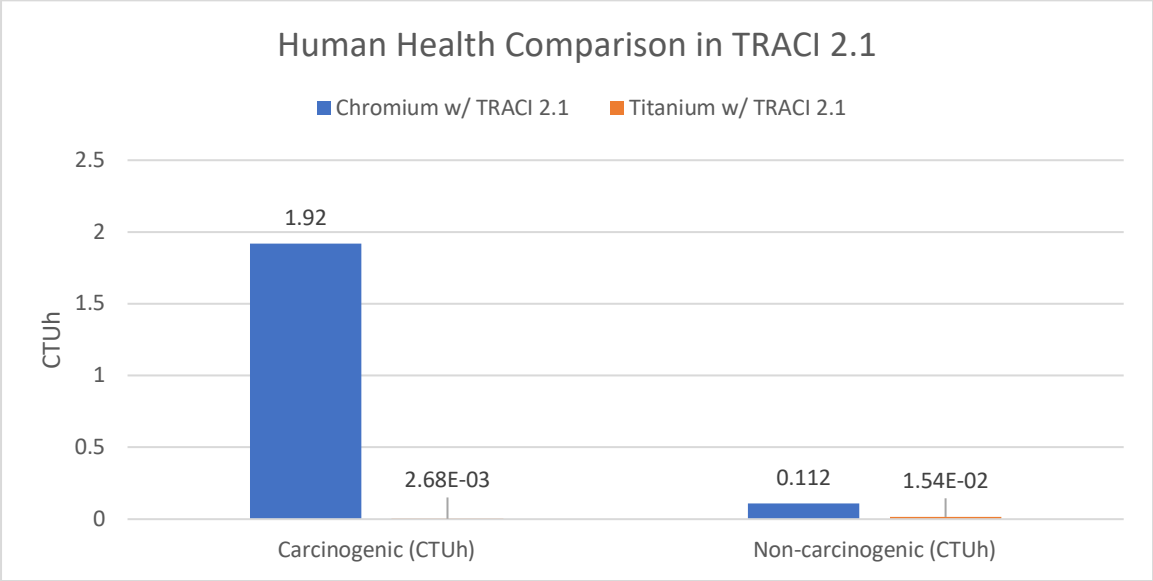


Figure III-5: Carcinogenic and non-carcinogenic harm

Chromium vs. Titanium

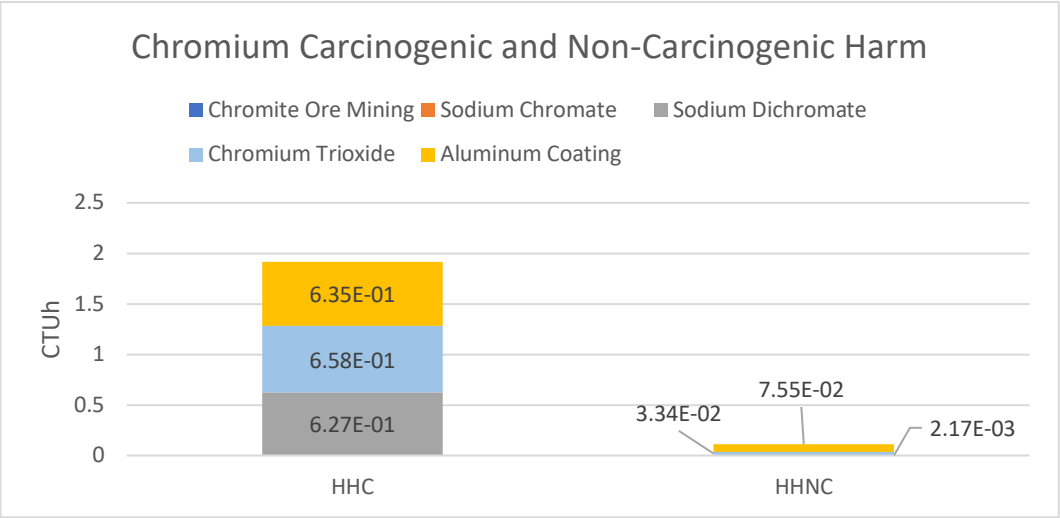


Figure III-6: Chromium human health impacts by process step

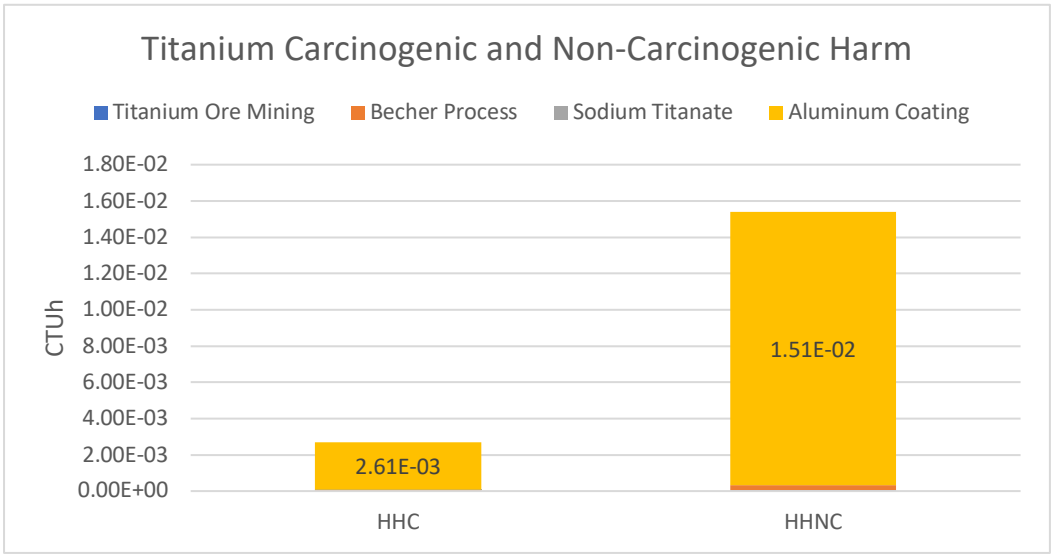


Figure III-7: Titanium human health impacts by process step

Further, while both products yielded high amounts of ecotoxicity, chromium's was significantly higher at 1.69 x 10^7 while titanium was at 2.78 x 10^5 CTUe as seen in Figure III-8. Chromium's ecotoxicity was mostly from the hexavalent chromium itself. The aluminum anodizing step was the most ecotoxic step in the chromium process with a contribution of 6.25 x 10^6 CTUe seen in Figure III-9. Sodium dichromate was a close second with 6.22 x 10^6. The significant ecotoxicity in these steps is mainly due to the significant amount of hexavalent chromium waste emitted during these steps. As with human health effects, titanium's ecotoxicity was not from titanium itself. Rather, the majority of ecotoxicity was from the processes for heat and electricity in anodizing process which alone accounted for 2.69 x 10^5 CTUe of the total 2.78 x 10^5 (Figure III-10).

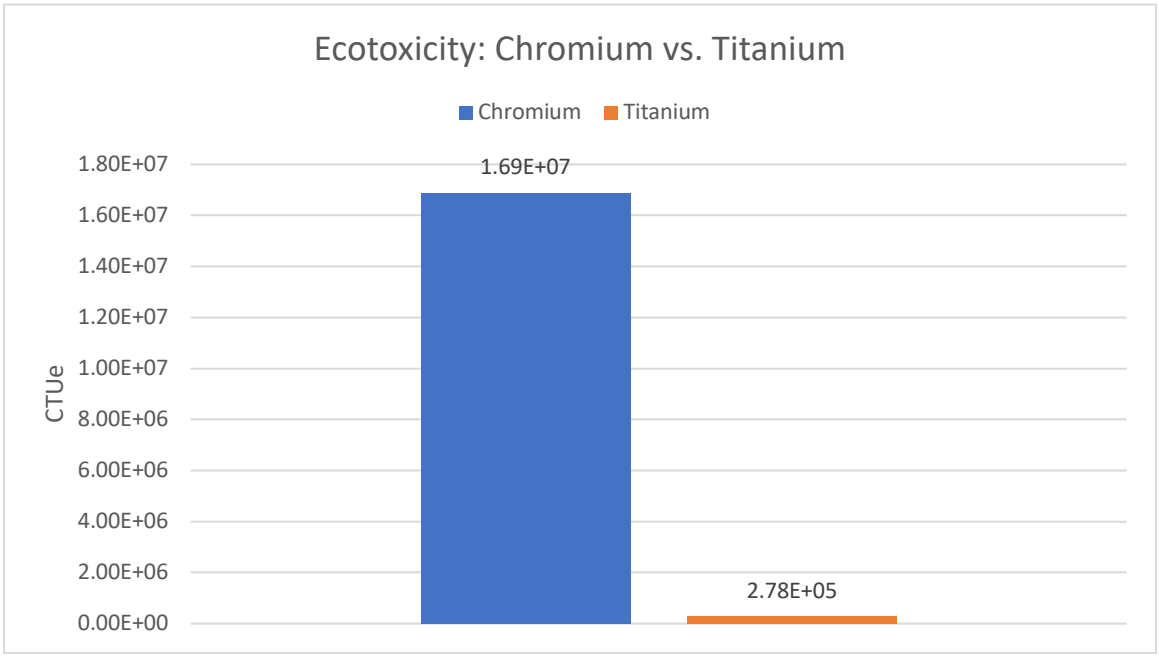


*Figure III-8: Ecotoxicity CTUe (PAF*m³ *day/kg) chromium vs. titanium processes*

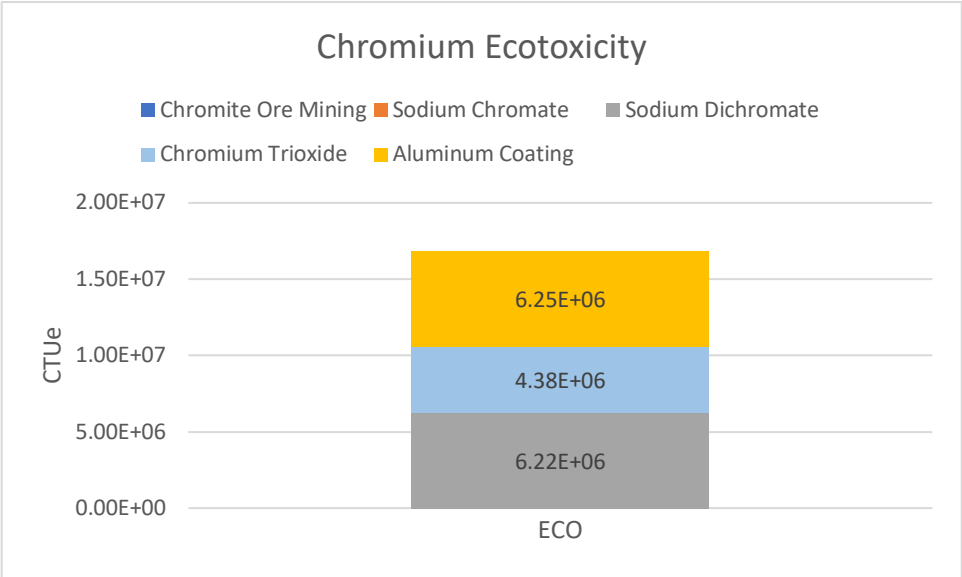


Figure III-9: Chromium ecotoxicity by process step

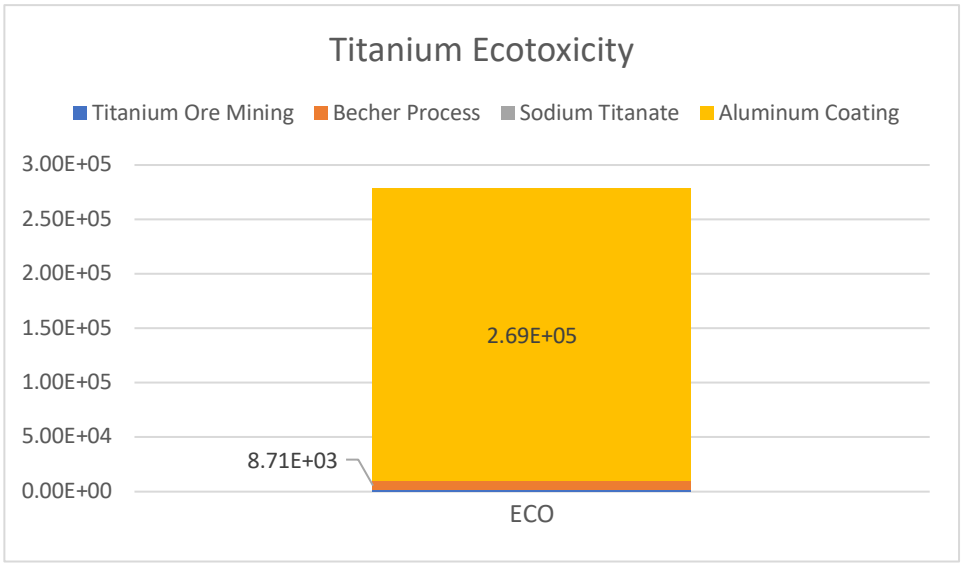


Figure III-10: Titanium ecotoxicity by process step

All other impact categories were similar with titanium bettering chromium slightly in all categories except global warming potential (CO_2 emissions). Higher CO_2 for titanium is most likely due to the requirement of coal for the Becher process while chromium had no coal inputs. All impact categories for chromium (blue) vs. titanium (orange) comparisons are normalized and shown in Figure III-11. Step by step impact contributions for both chromium and titanium can be seen in Figure III-12 and Figure III-13. Since the anodizing process is dominant in both scenarios, Figure III-14 and *Figure III-16* help gain insight to the impact distribution of actually manufacturing the chromium and titanate coatings without the anodizing step. An important observation for these graphs excluding the anodizing step are the significant impacts of the chromium manufacturing processes that directed relate to emissions of the hexavalent chromium. Conversely, for titanium the major impacts come from the higher energy requirements from mining compared to chromium, and the energy required for the Becher process.

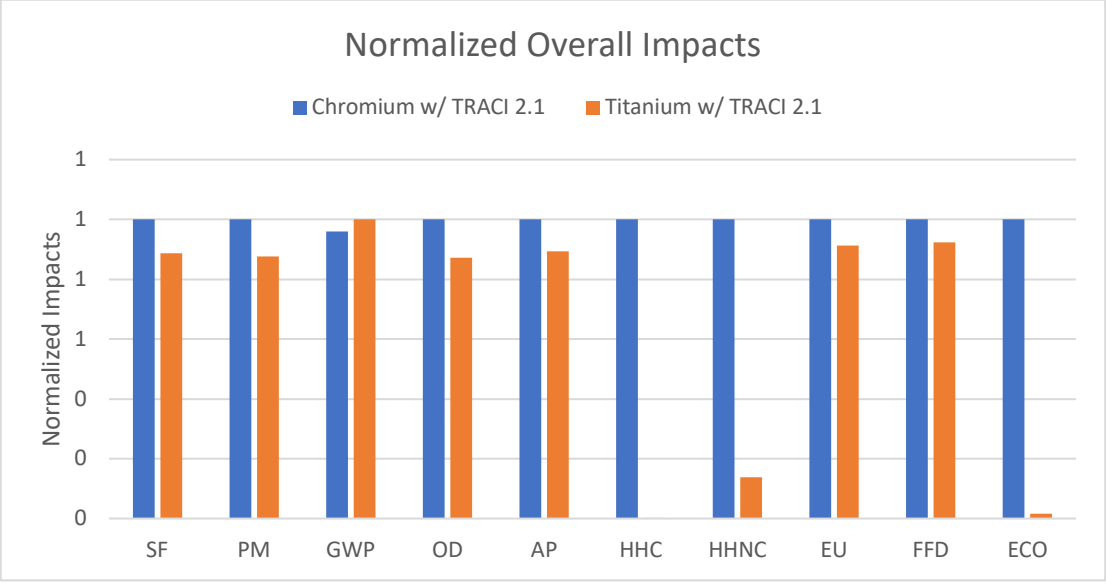


Figure III-11: Normalized impact results

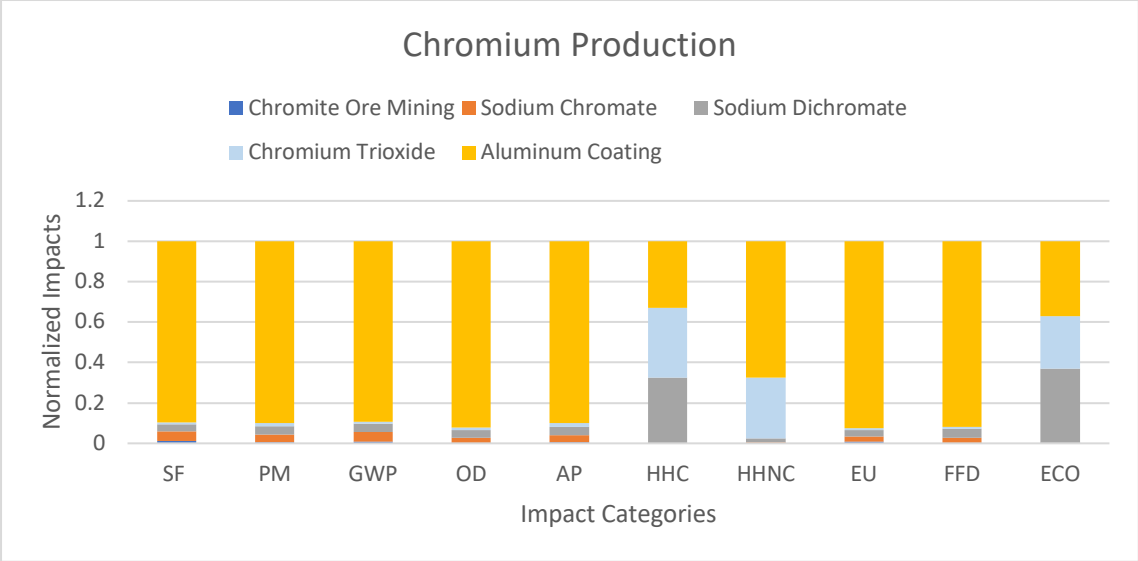


Figure III-12: Chromium Process breakdown of normalized impacts

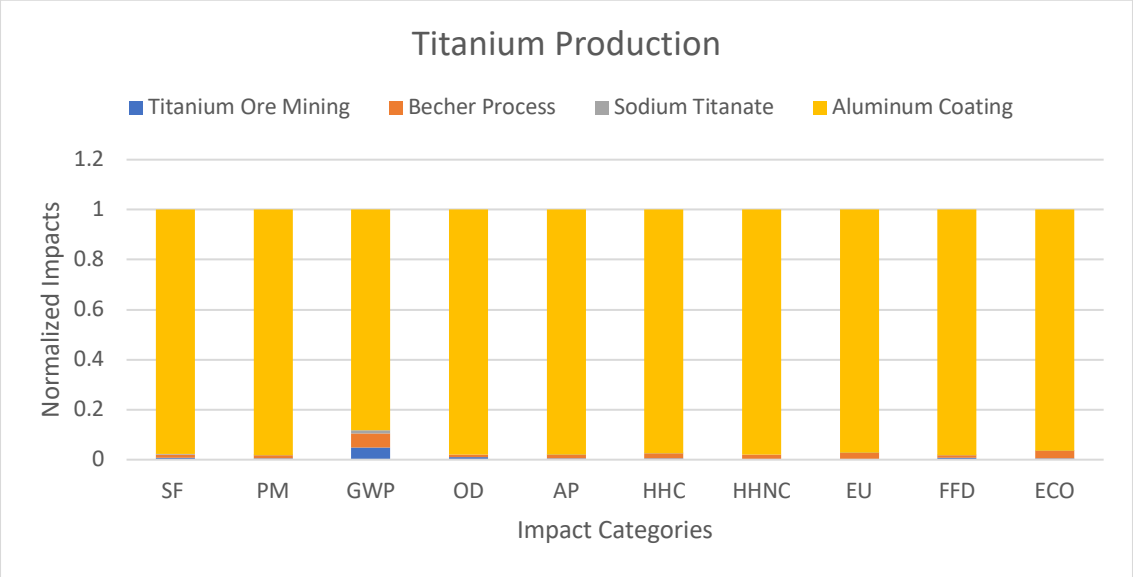


Figure III-13: Titanium Process breakdown of normalized impacts

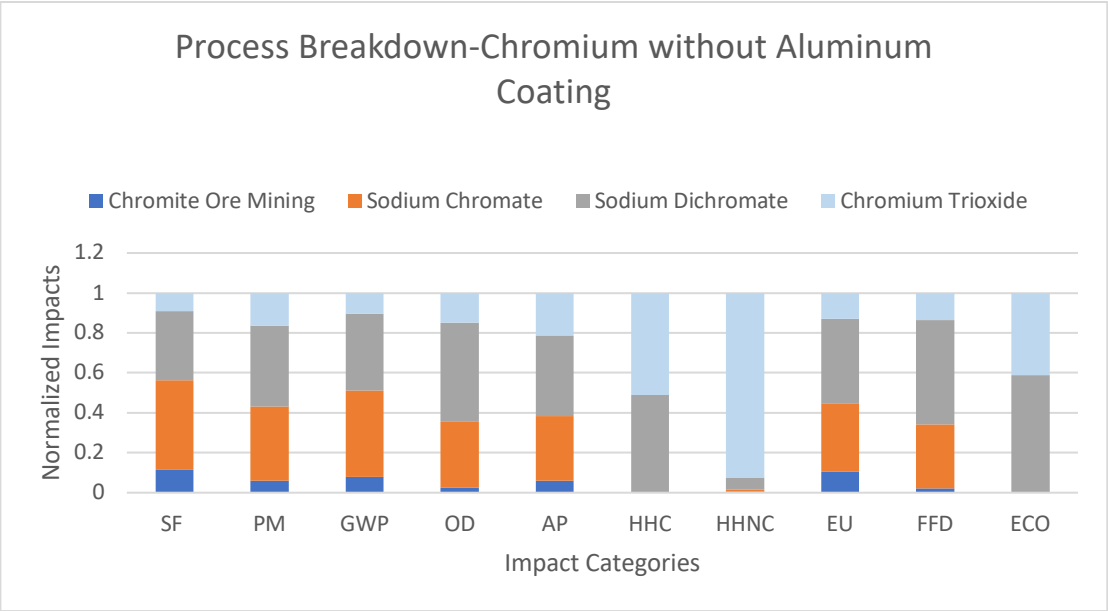


Figure III-14: Chromium normalized impact breakdown without anodizing

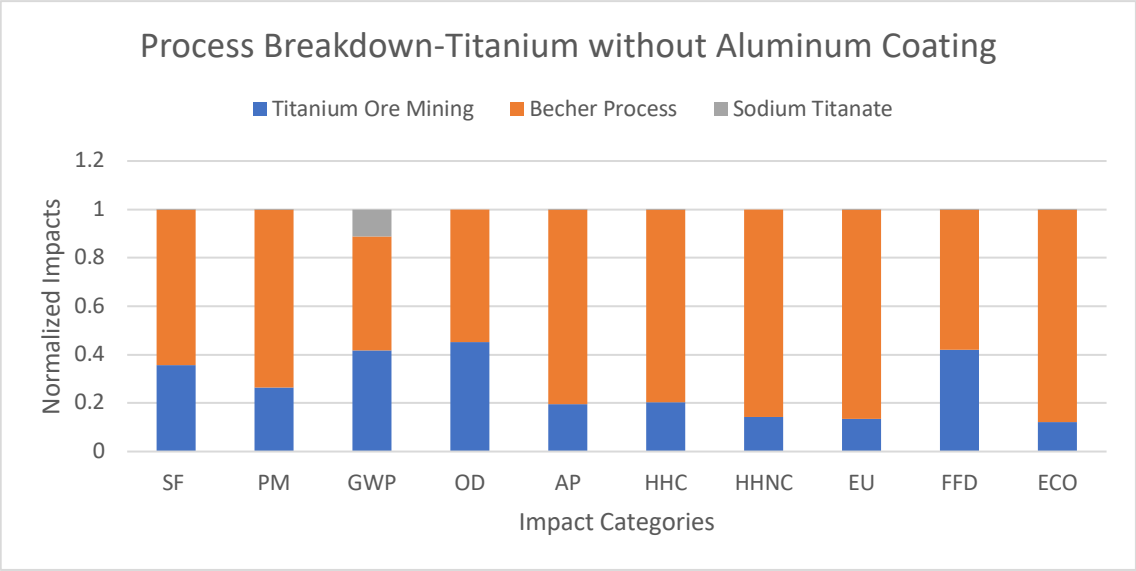


Figure III-15: Titanium normalized impact breakdown without anodizing

3.4 Interpretation

3.4.1 Significant Issues in LCA

The modeling of this LCA required various processes and flow stages because of all the steps required to get chromium ore and titanium ore to a final product that can be used for coating. The chromium LCA was easier to model because energy requirement data was taken directly from the Harscoet and Froelich paper previously conducted on a hexavalent chromium LCA. The paper had covered every step's energy and raw material demands as well as every emission to get chromium from ore to usable chromium trioxide. The paper pulled their own data from working closely with a factory that produced hexavalent chromium and thus, the data is thought to be high quality and containing low uncertainty. (Harscoet & Froelich, 2007)

However, while studies on LCAs of titanium dioxide were found, few papers included any energy, raw materials, or emissions numbers (Gázquez, Bolívar, Garcia-Tenorio, & Vaca, 2014). Moreover, a paper was found on the final step of synthesizing titanium dioxide into sodium titanate; but there were no mass numbers given for the process (Stenina, et al., 2016). Papers written by government agencies such as the USGS and ARPA-E were found to contain electric requirements and CO_2 emissions from the entire titanium dioxide production process (USGS, Estimates of Electricity Requirements for the Recovery of Mineral Commodoties, 2011) (ARPA-E). This led to total CO_2 emissions being divided evenly between the number of processes to try to fairly model the system. Further, the starting titanium ore mass was matched to the starting chromium ore mass (2825 kg) from the chromium LCA paper (Williams, 2011). This was possible

as both had similar percentages of the metal within the ore and could be thought to provide similar amounts of product further down the line (USGS, Mineral Resources Program, 2019).

To calculate mass inputs of various other raw materials and energy throughout the titanium process, mass balancing was used. This was chosen as the best option to get a close estimate of how much of each would be needed to properly react with the titanium. While efforts were taken to model the titanium as fairly as chromium, there could be uncertainties in the data as no direct numbers were found from industry.

3.4.2 Sensitivity

Steps were taken to model the accuracy of the LCA. One area that was thought to possibly skew data was transportation. Chromium is almost exclusively mined outside the U.S. and South Africa is one of the largest mine producers of chromium (Coalition, 2019). On the other hand, titanium is found throughout the U.S., as close as North Carolina (Titanium in the Old Hickory Mineral Sand Deposit, 2016). Transportation inputs were modeled from mine to manufacturer and finally to Clemson as a final destination. The original comparisons of the processes used these different distances to model realistic data. However, to examine an almost exact transportation between both products, a second analysis was run showing titanium as travelling the same distance as chromium.

At first this change in transportation was hypothesized to drastically alter the titanium impacts for the worse and make the chromium and titanium processes more comparable. Yet, the changes in distances ended up have little effect on the final impacts. These results can be seen in Figure III-16 which compares normalized impacts of titanium with the same distance as chromium to titanium with the assumed distance from North Carolina. This figure also includes the original chromium impact results for comparison. An observation of this graph shows every impact category was higher or equal when titanium had the same transportation distance as chromium as compared to titanium from N.C.; however, the difference was minimal. This result indicates transportation distance is a small factor in the overall impacts of these two processes. This conclusion was supported by the emissions breakdown of CO_2 within the openLCA

program. The increase in CO_2 emissions when titanium was transported from South Africa was only on the order of 4.3×10^2 kg. Overall, this provided a barely visible difference as total CO_2 emissions for titanium originally was 1.51×10^5 kg. Therefore, this further confirms titanate as a significantly better compound for humans and the environment regardless of distance from mine to manufacture. Lastly, it can be seen that chromium still loses 9/10 categories regardless of titanium transportation distance.

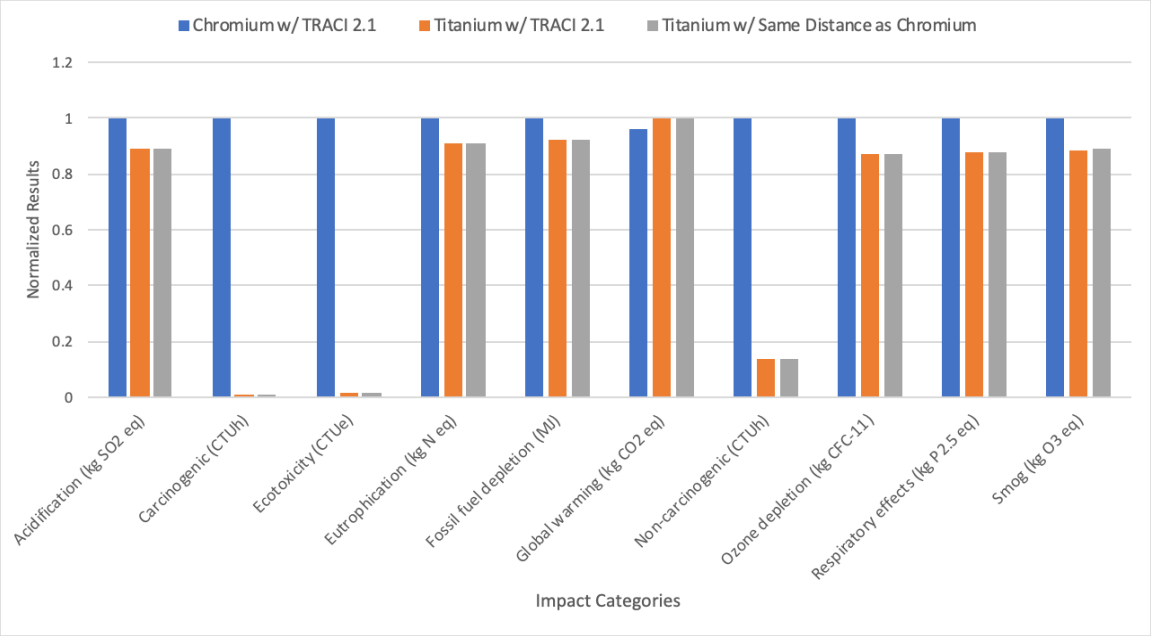


Figure III-16: Titanium same distance as chromium normalized impacts

A second test of sensitivity was done by comparing two impact analysis programs to see if there were drastic differences in reported impacts. As stated, the impact assessment program used for the main assessment of this project was TRACI 2.1 which was created by the EPA. To perform a sensitivity analysis on impact assessment software

a second program called USEtox 2 was chosen. USEtox 2 is a program that was created by collaborating researchers from both the U.S. and Europe (USEtox, 2020). It is largely used for European applications but is a sufficient program for the U.S. as well. USEtox is a non-profit organization of independent scientists and engineers and thus was chosen to provide a quality comparison with TRACI 2.1 which is a government run program. (EPA, LCA: Principles and Practices, 2006)

The sensitivity analysis between the two programs provided similar impact results for carcinogenic and non-carcinogenic effects. USEtox 2 gave slightly lower amounts for chromium and titanium in both cancer and non-cancer human health categories. However, USEtox 2 yielded extremely higher amount for the ecotox category for both compounds. Titanium especially had a much higher ecotoxicity value for USEtox 2 than from TRACI 2.1. Yet, despite titanium's significant difference in ecotoxicity, the most important observation was both methods show titanium as the clear winner regardless. It is not known why there is a sizable difference in ecotoxicity values for both compounds when moving from one impact program to another. At this time the hypothesis is USEtox 2 puts a more significant weighting factor on ecotoxicity as compared to TRACI 2.1. The results of this sensitivity analysis can be seen in Figure III-17, Figure III-18, and Figure III-19.

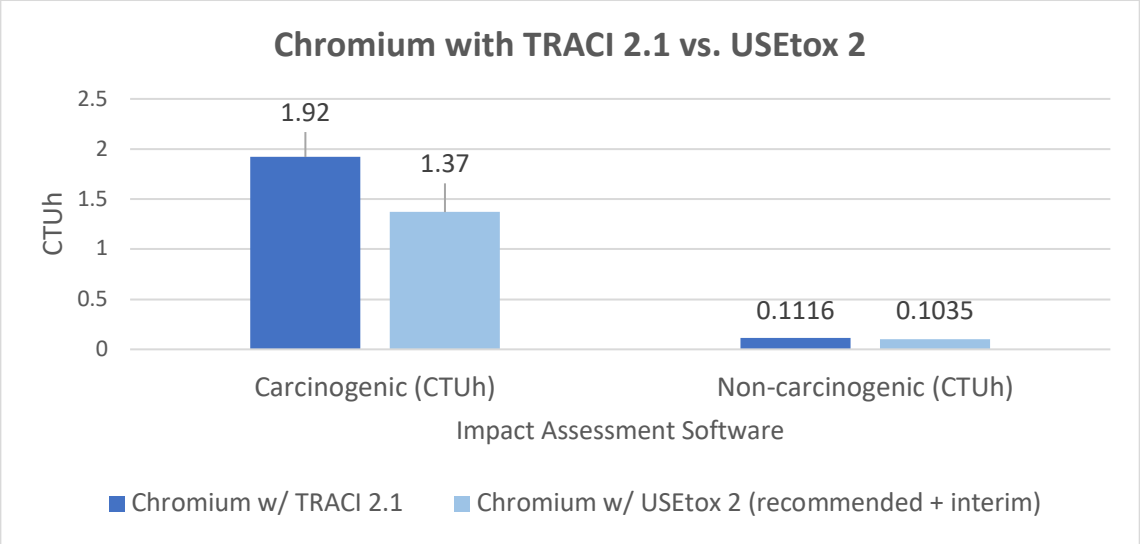


Figure III-17: Chromium carcinogenic and non-carcinogenic impacts

TRACI 2.1 vs. USEtox 2

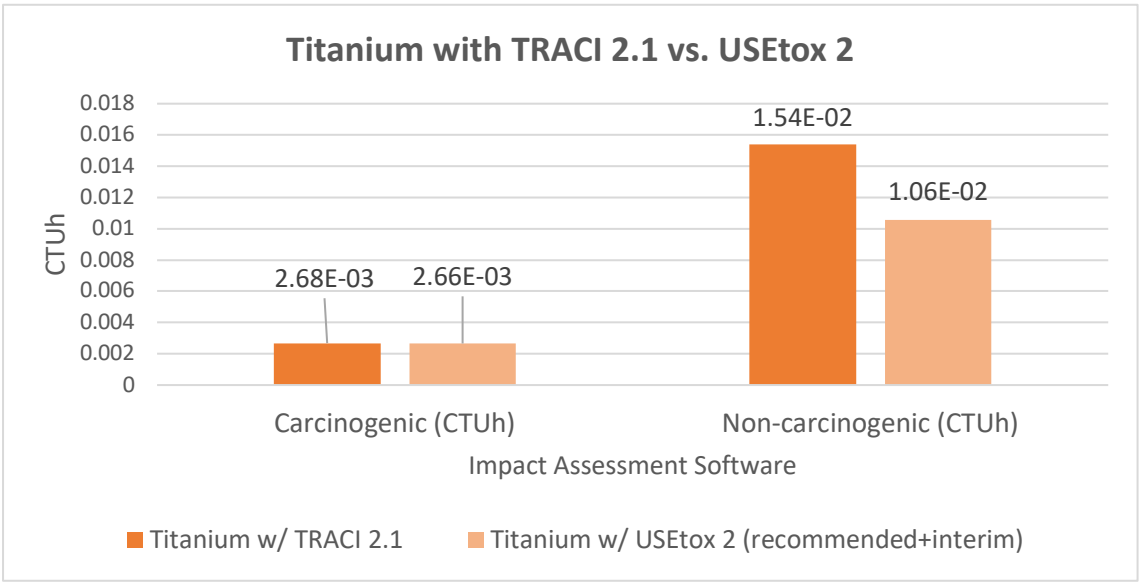


Figure III-18: Titanium carcinogenic and non-carcinogenic impacts

TRACI 2.1 vs. USEtox 2

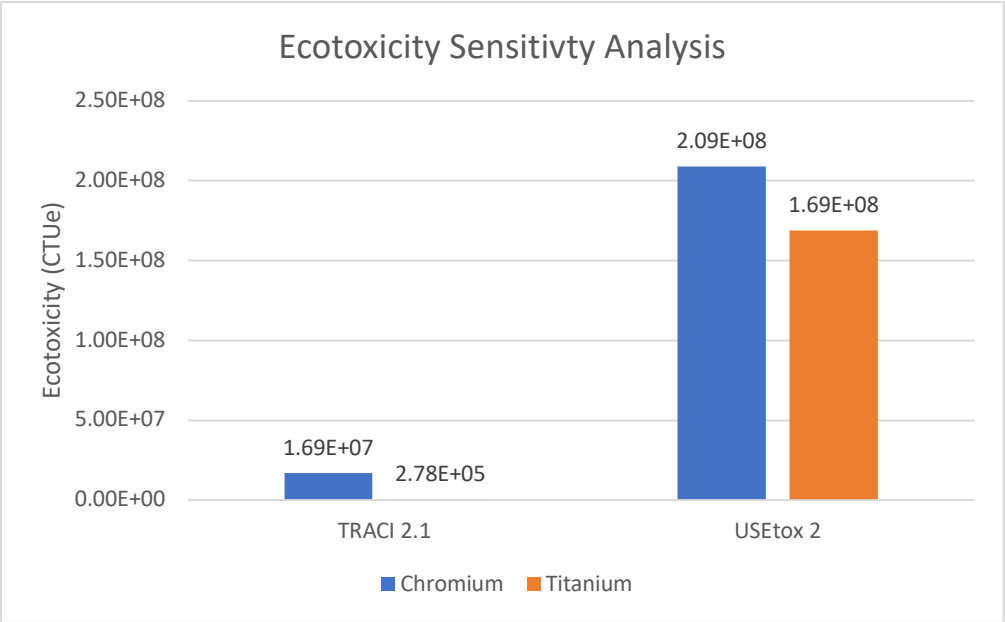


Figure III-19: Ecotoxicity: TRACI 2.1 vs. USEtox 2

3.5 LCA- Conclusion and Future Work

This LCA supported the hypothesis that titanium-based (titanate) compounds would be significantly better for the environment and human health than chromium-based compounds. The results showed substantially lower values for the titanium process in the main categories of focus: human health carcinogen and non-carcinogen, and ecotoxicity. To fully understand this reduction of impact values it is important to multiply the impact values (impact value/kg) by recent TRI emissions data from primary and fabricated metal manufacturing in South Carolina.

In 2016 alone, 135,648 kgs of hexavalent chromium emissions were released into the environment from primary and fabricated metal manufacturing within South Carolina (TRI, 2019). The findings from the LCA showed Cr (VI) emissions could possibly cause cancer in roughly two (1.92) people per kg released into the environment. This would mean roughly 271, 296 people have a chance of developing cancer in their lifetime from the 2016 Cr (VI) emissions. To be clear, this value is significantly higher than the actual number of individuals who would develop cancer from these emissions. However, it is important to compare this value with the possible individuals who may develop cancer due to emissions from the titanium-based process. The LCA showed 3.0×10^{-3} people could develop cancer per kg of emissions from the titanate process. When this number is multiplied by the same emission mass of 135,648 kg, only 407 people may be affected by cancer caused by these emissions. Putting these impact values in perspective aids in fully

understanding the overall differences in the carcinogenic and toxic ability of hexavalent chromium and titanate.

Moving forward, further research should be conducted comparing both the chromium and titanium production process and the actual application of titanate in place of chromium. In the future titanium oxide derived coatings must be implemented on an industrial scale to study their feasibility and anti-corrosive ability in a practical setting. At present this research hopes the known detrimental effects of hexavalent chromium will continue to push research in the right direction and lead to a more sustainable future where cancer causing compounds are not readily used in industry.

CHAPTER FOUR

IV. RISK ASSESSMENT

4.1 Overview

A significant part of assessing chromium emission impacts in the state involves understanding the possible human and ecosystem health impacts of exposure near emission sites. Hexavalent chromium pollution can be emitted through air or water releases that can directly affect the surrounding population. It is important to be able to assess the possible risk to human health from these emissions. Thus, it was decided to conduct a risk study for the Charleston metropolitan area. Two of the largest Cr (VI) direct water emission sites in S.C. are in close proximity to major fishing areas and the main drinking water reservoir for the Charleston area (Bushy Park Reservoir) (GoogleEarth, 2019). According to Fjeld et al., 2007, a risk assessment is "the process of making a quantitative estimate of the human health risks resulting from the release or potential release of contaminants to the environment" (Fjeld, Eisenberg, & Compton, 2007).

4.1.1 Motivation

Recent peer-reviewed studies have concluded that the Federal EPA's current federal regulations on maximum contaminant level (MCL) for total chromium in drinking water of 0.1 mg/L is higher than it should be to protect human health (OEHHA, 2011). Moreover, in 2019 the WHO published a MCL of 0.050 mg/L (50 ppb) for total

chromium and concluded concentrations above this would be cause for concern (WHO, 2019). The WHO based this MCL on "achievability by current treatment technologies, measurability by analytical methods, and toxicology" (WHO, 2019). However, both MCL values have been contested by both state level EPA's and independent organizations of scientists, engineers, and toxicologists (OEHHA, 2011) (Norris, 2016). These researchers believe limits for drinking water concentrations need to be set specific to Cr (VI) because of the variability in possible harm when setting a value based on total chromium. The vast differences in toxicity and carcinogenicity between the two require closer observation of the species present in the water (ATSDR, 2011).

Both the EPA and WHO have state that testing specifically for Cr (VI) would not be feasible; however, an EPA study conducted from 2013-2015 reported testing water specific to chromium in its hexavalent form (EPA, Monitoring Unregulated Drinking Water Contaminants, 2016). Despite this, the Federal EPA continues to utilize MCL levels calculated nearly three decades ago in 1991 and 1992 referring only to total chromium (IRIS, 2010). In 2010 the EPA released a draft assessment for a new study on hexavalent chromium's possible effects from the oral ingestion route. In 2011 the majority of independent peer reviewers concluded that the oral cancer slope factor calculated was "*accurate and concise*" and that hexavalent chromium "*is likely carcinogenic to humans by the oral route of exposure"* (IRIS, 2010). Despite these conclusions the EPA has never republished an official report on new federal regulation for Cr (VI) MCL.

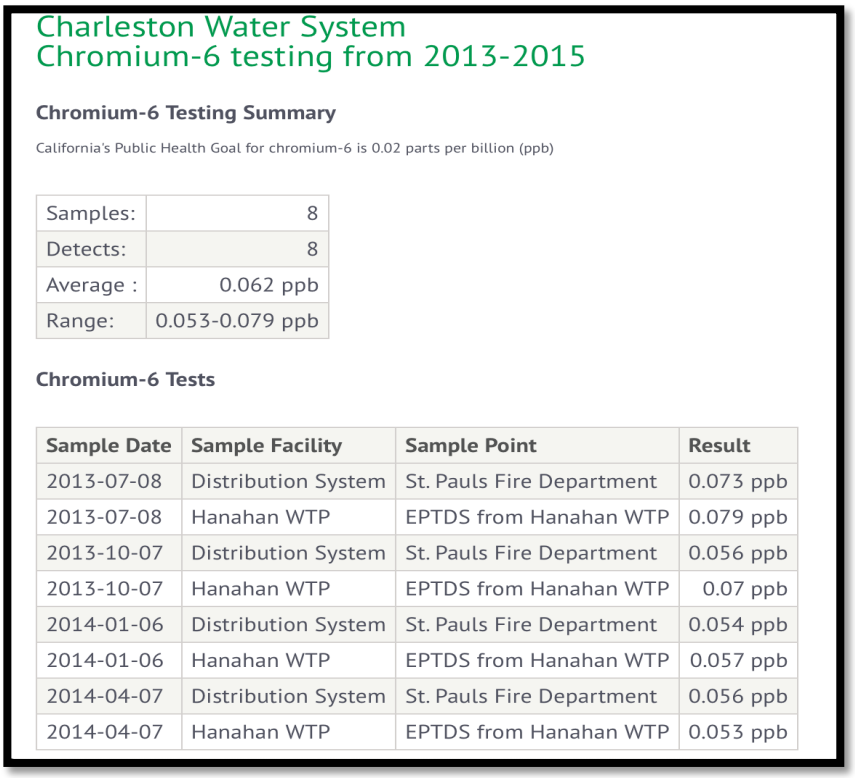
In 2016 the EPA stated that their final review would be published to the public in 2017, but currently there are still no updates on this publication. This delay has persisted despite knowledge of studies done by the National Toxicology Program in 2008 that showed clear dose-response relations in rats and mice that ingested water with traces of hexavalent chromium (NTP, 2008). Moreover, in 2011 the California EPA's Office of Environmental Health Hazard Assessment released a peer-reviewed report focused on attaining a safe level of hexavalent chromium in drinking water (OEHHA, 2011). This report called for a new Public Health Goal (PHG) MCL of 0.02 ppb (0.02 μg/L). OEHHA concluded that any concentration above this limit would affect an individual's chance of developing cancer. This 0.02 ppb value is 5,000 times lower than the MCL enacted federally by the EPA for total chromium that is still the standard today.

A further concern relates to a recently published EPA report performed under the Unregulated Contaminant Monitoring Rule (EPA, Monitoring Unregulated Drinking Water Contaminants, 2016; IRIS, 2010). Under this rule, every few years the EPA chooses certain chemicals to test for in public drinking water systems (PWS) that are not directly tested for under the Safe Drinking Water Act (SDWA) of 1996. This is performed to recognize which new contaminants might need to have further regulation in drinking water. From 2013-2015 the EPA conducted tests at 4,919 PWS to find concentrations of hexavalent chromium in effluent water. Out of these 4,919 systems, 4,401 tests yielded hexavalent chromium concentrations of higher than 0.03 ppb which was the set minimum reporting level (MRL) for the study. Thus, roughly 90% of PWS contained levels of Cr (VI) above the California EPA's recommended level of 0.02 ppb.

This result is striking considering the California EPA's conclusion that any level above 0.02 ppb would lead to the possibility of developing cancer.

In this report the Charleston Water System (CWS) drinking water tested 2 to 4 times higher than the Public Health Goal of 0.02 ppb (EPA, Monitoring Unregulated Drinking Water Contaminants, 2016). The tests conducted at the Hanahan Treatment Plant (main receiver of CWS Bushy Park Reservoir intake water) showed an average hexavalent chromium concentration of 0.065 ppb (Figure IV-1). This is more than three times higher than the recommended Public Health Goal.

As water is treated at a plant, some mass of hexavalent chromium in the influent water will be taken out of the system as Cr (VI) may get reduced to Cr (III) and removed by flocculation, sedimentation, and various filtration processes (SUEZ, 2020). Thus, it is likely that higher concentrations of chromium are present in the influent water from the reservoir. These higher concentrations in the influent point toward a sizable infiltration of hexavalent chromium into the reservoir from anthropogenic sources. Moreover, the EPA test samples confirm that hexavalent chromium is reaching the drinking water of almost 800,000 Charleston area citizens (CRDA, 2020). This statistic requires the attention of scientists and engineers and was an inspiration for this research.



Charleston Water System
Chromium-6 testing from 2013-2015

Chromium-6 Testing Summary

California's Public Health Goal for chromium-6 is 0.02 parts per billion (ppb)

Samples:	8
Detects:	8
Average :	0.062 ppb
Range:	0.053-0.079 ppb

Chromium-6 Tests

Sample Date	Sample Facility	Sample Point	Result
2013-07-08	Distribution System	St. Pauls Fire Department	0.073 ppb
2013-07-08	Hanahan WTP	EPTDS from Hanahan WTP	0.079 ppb
2013-10-07	Distribution System	St. Pauls Fire Department	0.056 ppb
2013-10-07	Hanahan WTP	EPTDS from Hanahan WTP	0.07 ppb
2014-01-06	Distribution System	St. Pauls Fire Department	0.054 ppb
2014-01-06	Hanahan WTP	EPTDS from Hanahan WTP	0.057 ppb
2014-04-07	Distribution System	St. Pauls Fire Department	0.056 ppb
2014-04-07	Hanahan WTP	EPTDS from Hanahan WTP	0.053 ppb

Figure IV-1: Charleston Water Cr (VI) levels

Finally, these oral routes of an exposure can also directly come from consumption of contaminated animals or plants. Hexavalent chromium does not readily partition to plants, but like other heavy metals it does bioaccumulate in fish. As the Cooper River is a major fishing river it is vital to understand the risks involved with consuming fish caught in this area (Burleson, 2020). Moreover, regardless of human health effects, the impact on fish and aquatic ecosystems must be recognized as well.

4.1.2 EPA RSEI

It is important to note that the EPA does already have some tools in place to help understand the possible risks generating from a certain reporting site. The EPA tool is the Risk Screening Environmental Indicators (RSEI) tool (EasyRSEI, 2020). This tool calculates "risk scores" for TRI reporting facilities based on the TRI data submitted. These scores are calculated by considering the size of the release, the fate and transport of the chemical, the size and location of the exposed population, and the chemical's toxicity. The EPA stresses that this tool does not conduct an actual risk assessment where clear data would be provided for dose, concentration, exposure, and risk. Rather, RSEI scores are unitless measurements meant to be observed in comparison to one another. For example, one company may have a RSEI score of 4,000 while another has a score of 2,000. The facility with the higher score has a more significant impact on humans and the environment.

The RSEI's lack of clear dose and risk data led to the conclusion that a risk assessment must be conducted to understand the possible effects of the studied chromium emissions. Risk data with defined units allows the audience to better understand and interpret potential impacts of chromium releases. Furthermore, a clear and concise display of data generates more interest into the problem at hand. With this in mind, it was decided to run a risk analysis of the two sites in South Carolina that directly release the most chromium into surface water within the state.

4.1.3 Sites of Interest

The two sites analyzed in this risk assessment both lie on the Cooper River, north of Charleston, SC. These sites are the Nucor Steel plant and the BP Chemical plant in Berkeley, South Carolina. The Cooper River is a major tributary into the Charleston Harbor area that is commonly used for industry (TRI, 2019), fishing (Burleson, 2020), and drinking water (Conrads, Petkewich, Falls, & Lanier, 2017). The Nucor plant is roughly 23 miles upriver from Charleston harbor while the BP facility is 13 miles upriver. The close proximity of these sites to one another, and a population of roughly 788,000 people in the Charleston metropolitan area, increases the possible harm caused by the addition of their emissions and makes these sites an excellent case study (CRDA, 2020). TRI data was again used for the emissions in this risk assessment. Emissions were observed over a 10-year period of most recent data from 2007-2016 (TRI, 2019).

Over this period the Nucor Steel plant was the largest total chromium release source in the state (water, air, and land application combined) with close to 391,000 kg of chromium released over a the observed 10-year time (TRI, 2019). Moreover, the Nucor Plant reported directly releasing a total of 655 kg of hexavalent chromium into the Cowbell Branch and Cooper River. This yields an average of roughly 70 kg per year. Similarly, the BP Chemical facility had the highest amount of hexavalent chromium emissions directly to surface water at a total of 1027 kg in a 10-year period. This yields an annual average of 103 kg being directly dumped into the Cooper River. Thus, a combined average mass of 173 kg of chromium was dumped per year between the two facilities.

The case for serious concern here comes from the Cooper River's previously mentioned characteristics as a major fishing and drinking water source. The mild climate of Charleston allows for river fishing all year long and the Cooper is one of the most sought-after destinations for local, national, and even international fisherman because of the wide variety of fish available and the sheer quantity found (Burleson, 2020). Since the Cooper is a tidal estuary river, it is home to fresh-water, salt-water, and diadromous species depending on the section of river and how far inland the tides reach each day. This high volume of fish leads to a high number of fishermen, many whom consume their day's catch. Fishermen can be seen along most areas of the Cooper River depending on what type of fish they desire to catch, which leads to a large area of possible exposure in the river (Fishidy, 2020).

A surprising statistic for fishing in the Cooper River is the lack of fish consumption regulations throughout the river. The South Carolina Department of Health and Environmental Control (SCDHEC) posts tables that display fish consumption advisories along various bodies of water within S.C. These advisories are typically based on tests for mercury and polychlorinated biphenyls (PCBs) because these compounds are known to bioaccumulate in fish and biomagnify in humans (SCDHEC, 2020). While chromium does not have the same biomagnification ability, several studies have shown its ability to bioaccumulate in fish and further in humans (Bakshi & Panigrahi, 2018; Aslam & Yousafzai, 2017). Further, as chromium bioaccumulates in fish and humans it is likely be present across a range of oxidation sites from +III to +VI. Therefore, chromium would likely not be bioaccumulating as purely Cr (VI) but rather in various oxidation

states depending on the reduction and oxidation reactions with the organism (Tchounwou, Yedjou, Patlollal, & Sutton, 2012).

Despite chromium's lower risk of biomagnification compared to mercury or PCBs, bioaccumulation within organisms has still be definitively linked to cause cancers in organisms (NTP, 2008) (Yousafzai et al, 2017). Yet, few fish consumption advisories are based on hexavalent chromium pollution in the U.S. One state that does provide consumption advisories based on Cr (VI) pollution is North Carolina according to the N.C. Department of Health and Human Services (NCDHHS) (NCDHHS, 2020).

According to TRI data, mercury and PCB releases along the Cooper River have been minimal over the time period of collected TRI data (TRI, 2019). Therefore, risk advisories are most likely low in the Cooper because of the lack of emissions of mercury and PCBs. However, fish should also be monitored for bioaccumulation of other heavy metals like chromium that are proven to build up in aquatic life (Yousafzai et al, 2017). The current rate of chromium releases in the Cooper should warrant an investigation into the bioaccumulation within the fish in that area. The focus on well-known biomagnification of compounds like mercury and PCBs can lead to overlooking a potential major fish contaminant such as chromium in this situation. The few advisories for fish consumption along the Cooper River can be seen in Figure IV-2. The only current advisories are for pickerel, largemouth bass, and mudfish. This is concerning considering the amount of industry along the river.

Cooper River	East Fork Cooper River Quinby Creek to The "T"	Chain Pickerel	1 meal a week
		Largemouth Bass	1 meal a week
		Blue Catfish	No Restrictions
		Bluegill	No Restrictions
		Bowfin (Mudfish)	No Restrictions
		Redear Sunfish	No Restrictions
		Spotted Sunfish	No Restrictions
		Warmouth	No Restrictions
	West Fork Cooper River From Lake Moultrie Dam to The "T"	Bowfin (Mudfish)	1 meal a week
		Black Crappie	No Restrictions
		Blue Catfish	No Restrictions
		Bluegill	No Restrictions
		Chain Pickerel	No Restrictions
		Largemouth Bass	No Restrictions
		Redear Sunfish	No Restrictions
		Warmouth	No Restrictions
	The "T" to Bushy Park	Bowfin (Mudfish)	1 meal a month
		Black Crappie	No Restrictions
		Blue Catfish	No Restrictions
		Bluegill	No Restrictions
		Chain Pickerel	No Restrictions
		Largemouth Bass	No Restrictions
		Redear Sunfish	No Restrictions
		Warmouth	No Restrictions
	Downstream of Bushy Park	Red Drum	No Restrictions
		Spotted Sea Trout	No Restrictions
		Southern Flounder	No Restrictions
		Striped Mullet	No Restrictions

Figure IV-2: Cooper River Fish Consumption Advisories (Mercury) (SCDHEC, 2020)

Similarly, the possible effect on drinking water is a major concern. The Bushy Park Reservoir is Charleston's main water source for over a half a million citizens and it regularly takes in water from the Cooper River (Conrads, Petkewich, Falls, & Lanier, 2017). This intake occurs at the Durham Canal which is located roughly 11 miles upriver from the Nucor Steel and 14.5 from BP as seen in Figure IV-3 below. The Charleston Water department source intake (CWS) is located at the southern end of the Bushy Park reservoir within 3 miles of both release sites and can be observed in Figure IV-3.

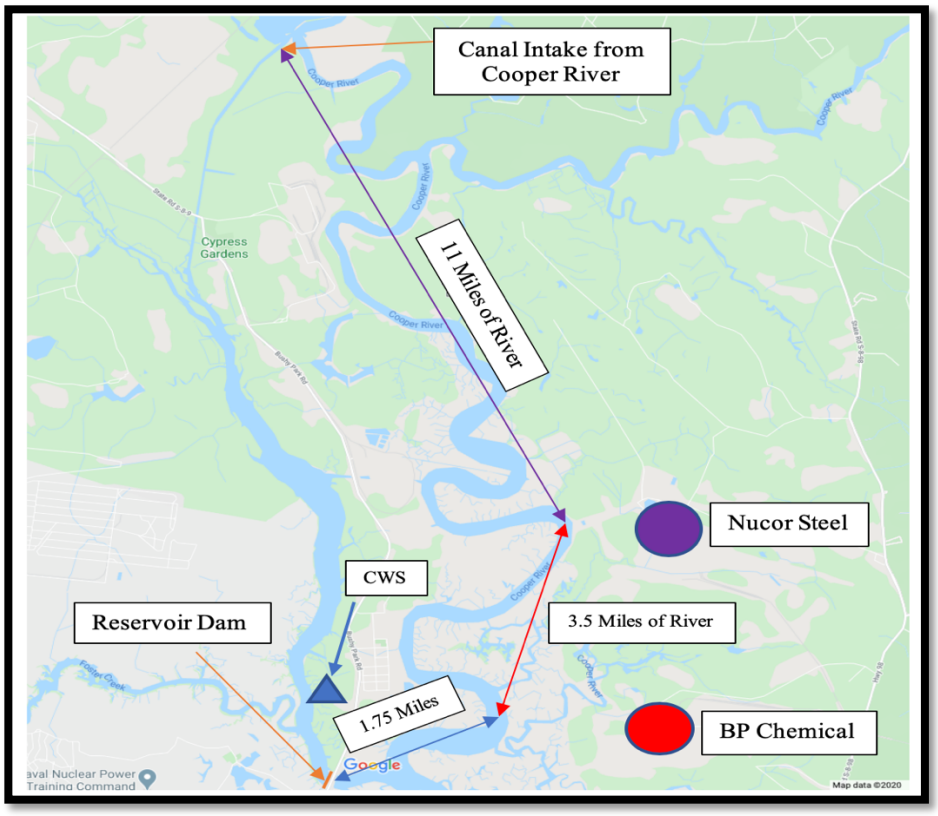


Figure IV-3: Map of Cooper River and Bushy Park Reservoir (GoogleEarth, 2019)

In an inland river flow upstream would not be of concern; however, the Cooper River is greatly affected by ocean tides and often reverses direction depending upon the tide. This reversal in flow could possibly lead to the movement of various pollutants from downriver back northward and eventually into the reservoir intake (NOAA, 2019). It is hypothesized that a minimal amount of hexavalent chromium would reach the intake because of the distance the pollutant would need to travel. However, during extremely high tides the water could push the bulk of the contamination plume further upriver and into the canal.

Related to high tides, another significant risk is the continuously increasing rates of both daily high tide and storm surge flooding in the Charleston metropolitan area (Charleston, 2020). The release sites of interest are in sections of the river that are still significantly affected by daily tides despite being more than 10 miles inland (GoogleEarth, 2019). The Bushy Park Reservoir and the Cooper River are separated only by a low-lying land barrier that is home to an industrial park. Thus, there is no significant elevated barrier to prevent flooding from the Cooper into the reservoir area. This would allow the hexavalent chromium being emitted directly to the east to easily flood into the drinking water reservoir.

Data from NOAA shows both the level of flooding from daily tides due to sea level rise and the occurrence of storm-based flooding events are exponentially increasing in the Charleston metropolitan area (NOAA Tides and Currents, 2020). In recent years 100-year floods have occurred on 5 or 10-year cycles and scientists are beginning to move away from using the 100, 500, and 1,000-year flood nomenclature (Hersher, 2019). A recently published NOAA report displayed the increasing frequency of high tide flooding in various coastal cities and territories owned by the United States (NOAA Tides and Currents, 2020). Figure IV-4 is a chart from this report that shows the recent increases in high tide flood frequencies. Observing Charleston's data, the frequency of high tide flooding has jumped from a consistent 0 to 3 days per year from 1950 to the early 2000's, to 8-10 days per year starting around 2010. NOAA states that by 2050 Southeastern coastal cities will encounter flooding from normal daily high tides roughly

85 days per year if rising sea levels continue at the same pace. By 2100 they estimate that Southeastern coastal cities could have high tide flooding *nearly every day of the year*.

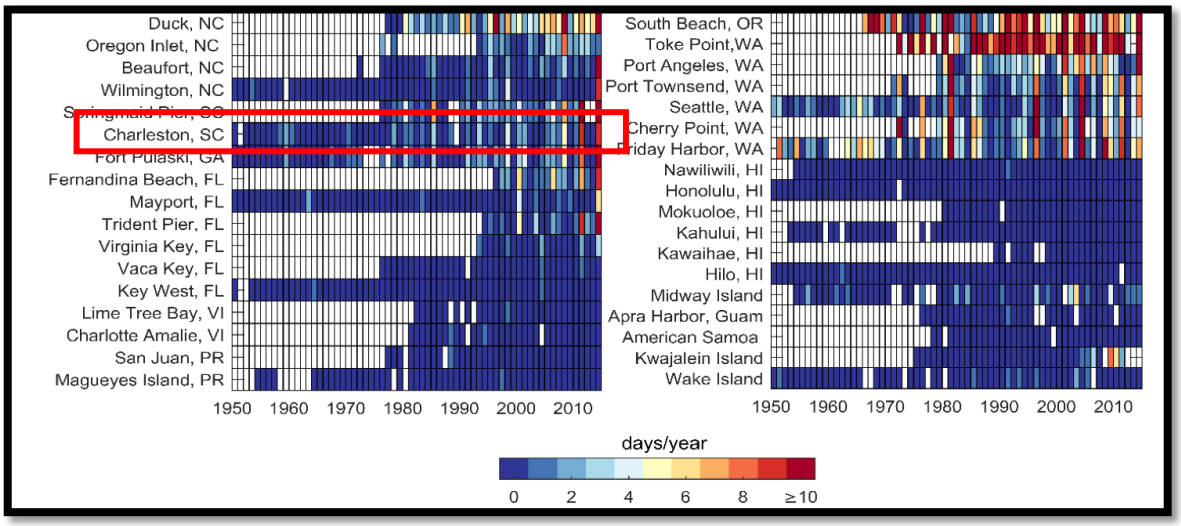


Figure IV-4: NOAA high tide flood frequency (NOAA Tides and Currents, 2020)

As climate change continues to increase sea levels, flooding likelihood continues to grow. In Figure IV-5 the FEMA created flood map images can be observed for the areas of interest (FEMA, 2018). These maps show most of the study area is at high risk of a 100-year flood (ever-more frequent than 1 in 100 in as time progresses) in blue shading. Most importantly, the land separating the hexavalent chromium release sites and the Bushy Park Reservoir are vulnerable to flooding and are considered high risk areas. Roughly a mile downstream from BP, the Cooper River and the reservoir are separated by a shallow dam called the Back River dam. Normally this dam protects the reservoir from mixing with the Cooper; but in major storm surges and hurricanes the Cooper can overflow into the reservoir. If Nucor or BP had released hexavalent chromium into the

Cooper River before a storm surge, it would not be difficult for significant amounts of chromium to enter the reservoir. This would likely lead to contamination of the reservoir following the flood event.

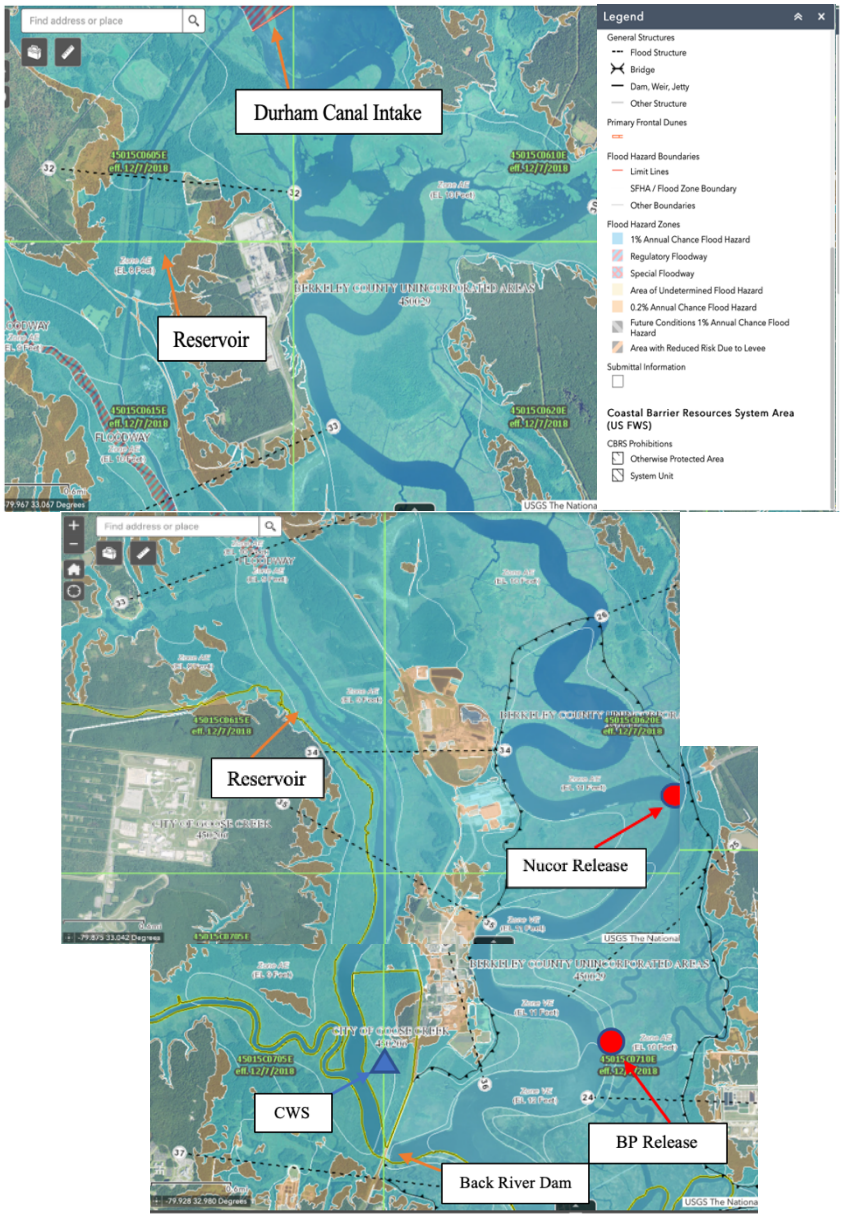


Figure IV-5: Flood map area of interest.

Blue shading is 100-year flood high risk zone (FEMA, 2018)

4.1.4 Cooper River

A significant part of any water transport risk model is understanding the body of water that the chemical is being released into. In order to understand the characteristics of the Cooper River, various informational sources were used to best quantify the Cooper River's ability to transport hexavalent chromium. The main area of focus for this assessment was between two points: the Durham Canal inlet point 11 miles north of the Nucor site and the Back River Dam 1.75 miles downriver of the BP site (GoogleEarth, 2019). This area was roughly the length of the reservoir and mostly contained high risk flood zones between the Cooper and the reservoir. Concentrations were calculated along this area as a function of distance and time.

The Cooper River is a large coastal plain river that spans roughly 48 miles from the outlet at the Charleston harbor up to the Pinopolis Dam (Engineers, 1977). It is an estuarine river that is greatly affected by ocean tides daily. This attribute allows the river to switch flow direction multiple times a day depending on the tides (Conrads, Petkewich, Falls, & Lanier, 2017) (NOAA, 2019). Thus, contaminants spilled into the river can be carried both toward the ocean and further upriver and inland. This ability to move in either direction adds complexity to fate and transport modeling of releases.

To measure the width of the river, google earth's measurement tool was used at various points. As mentioned, the Nucor Steel site is roughly 11 miles (17,703m) downriver from the Durham Canal intake while the BP Chemical plant is 14.5 (23,336m). The BP site is 1.75 miles (2798m) upriver from the Back River Dam while the Nucor site is 5.25 miles (8,463m). In total, the concentration of hexavalent chromium was measured

from the Durham Canal Intake to 11 miles downriver of the BP site. Overall this section of river observed is roughly 25.5 miles (41,038m) long.

The width varied from 149 to 574 meters depending on the section of the river measured (GoogleEarth, 2019). An average width was estimated from the Durham canal to 11 miles downriver of the BP site. This width was calculated by averaging 14 widths along this distance. The average width along these 25.5 miles was calculated to be 267 meters. Similarly, the average slope was calculated by google earth to be 0.004 m/m

over the 25.5 miles of river studied. (GoogleEarth, 2019)

The depth of the river was found via nautical charts from the National Oceanic and Atmospheric Administration (NOAA, 2019). These charts showed the varying depths of the Cooper River from the release sites to each endpoint. The depth of the river varied from 1 to 60 ft; however, an average depth was calculated to be 25 ft (7.62m) based on the frequency of depth measurements along the desired pathway.

Streamflow is another crucial factor in contaminant transport. Streamflow for the transport pathway was found through the United States Geological Society (USGS) flow data (StreamflowUSGS, 2019). A test site between the two release sites was chosen for streamflow data. The constant change in flow direction from tidal influence also created a wide variance of flow speed and thus total flow in either direction throughout a day's time. Data was provided for multiple days over a two-year period of observation. Flow data was chosen from the date within the dataset where the longest duration of streamflow data was recorded on a consistent interval. Although data was taken from one

day, all other data from varying dates had streamflow consistent with the flows recorded on the chosen date.

Flow varied from -60,500 ft^3/s (upriver) to +61,800 ft^3/s (downriver) in the observed USGS data at gauge site. Observed data showed a reverse in flow direction roughly every 5 hours of measured data. Flows could theoretically go as low as 0 when the tide changed the direction of flow. For this assessment flow was assumed to be at zero at time of release and a model was created for each flow direction as discussed in 4.1.5. Tidal flow with respect to time can be seen in Figure IV-6

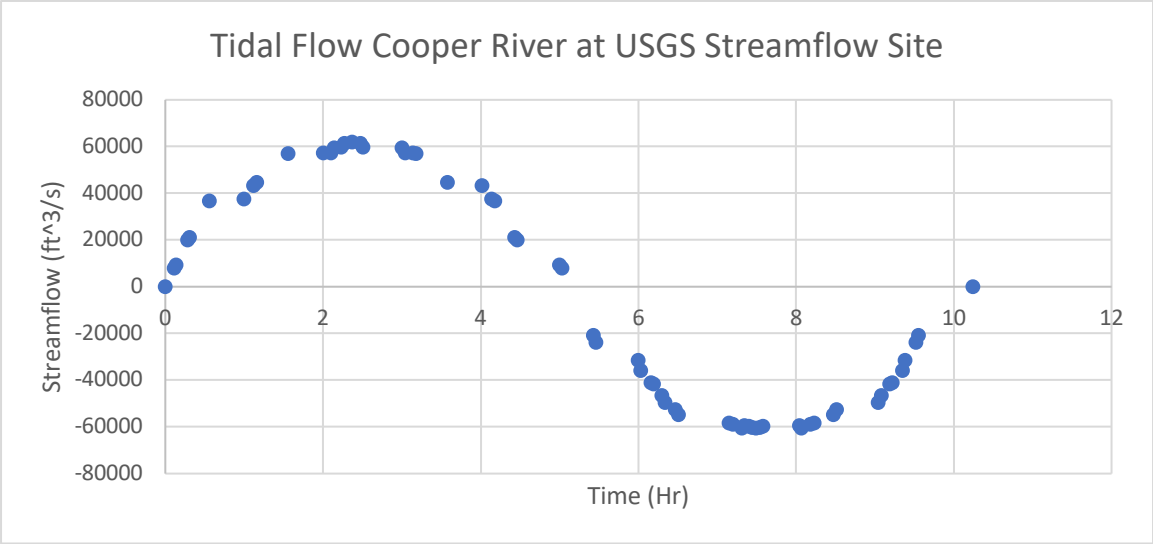


Figure IV-6: Cooper River Flow

with respect to time (StreamflowUSGS, 2019)

4.1.5 Assumptions

In this risk assessment hexavalent chromium transport from the release sites was modeled as a function of time and distance travelled. USGS data taken from river measurements between these two sites was used to understand daily tidal flows in the river (StreamflowUSGS, 2019). Concentrations at distances of 1, 2, 5, 7 and 11 miles were modeled for Nucor releases in the upriver direction. The Durham Canal sits at mile 11 north of the Nucor site and so it was determined to be the final important concentration site for the upriver models (GoogleEarth, 2019). Nucor releases downriver were modeled at 1, 2, 5.25, 7, and 11 miles as the Back River dam is at 5.25 downriver of Nucor. BP releases were modeled at 1, 2, 5, 7, and 14.5 miles because the canal is 14.5 north of BP. BP releases downriver were modeled at 1, 1.75, 5, 7, and 11 miles because the dam is 1.75 miles downriver.

A significant assumption for this model was a flow close to zero (<1 m^3/s) at the release site at the time of release. For flow downriver, as time since release increased flow increased until it peaked at low tide and then began to decrease back to zero. Flow in the downriver direction forms the positive curve of Figure IV-6 in section 4.1.4, while flow upriver forms the negative curve. When modeling flow upriver, the USGS flow values were reported as negative (-) values because the water was flowing in the reverse (upstream) direction. In order to use these values properly in the modeling equation they had to be multiplied by negative 1 to yield a positive value. After this was done these values were similarly taken with respect to time until peak flow was reached at high tide and began to decrease back to zero. Models were run this way to capture the maximum

possible concentration in one direction with the river flowing in that direction for the longest possible duration.

In tidal estuary rivers saltwater intrusion often has an effect on the coagulation and sedimentation ability of contaminant ions because of the common ion effect (Clark, 2019). Typically, an intrusion of saltwater would make a metal less likely to partition to suspended solids and stay mobile in water. This would likely lead to a higher contaminant concentration dissolved in water than sediment and would yield fairly different scenarios compared to freshwater. However, heavy metals like hexavalent chromium tend to have low distribution coefficients (K_d) and Cr (VI) has one of the lowest at 19 L/kg (Fjeld, Eisenberg, & Compton, 2007) (PANCHEMIE, 2020). For reference, other heavy metals such as Mercury and Cadmium have K_d's of 52 and 79 L/kg respectively. Similarly, other inorganic contaminants such as Uranium and Plutonium have K_d's of 450 and 4,500 L/kg. Since K_d equals concentration of solids phase divided by concentration dissolved, this means Cr (VI) does not partition readily to suspended solids and sediment even without salt present. This fact also explains the profound mobility that hexavalent chromium has in nature because it does not easily attach to soils. In fact, mass of contaminant sorbed and settled out was calculated to be below 1.0×10^{-15} $mg/s^{-1}L^{-1}$ even at total suspended solid levels of 1,000 mg/L. Therefore, since the mass of contaminant settling out is already negligible in freshwater, it was assumed saltwater intrusion would not have a significant effect on decreasing the amount of hexavalent chromium sorbing to solids. Moreover, these release sites are quite far

inland (> 10 miles) and while being affected by saltwater, the area was assumed not to have high concentrations of salt because of freshwater dominance in the studied area.

4.2 Risk Modeling

In this risk assessment multiple scenarios were considered to best understand the possible outcomes of released hexavalent chromium. To get a basic understanding of how a contaminant may move in this tidal river system NOAA's General NOAA Operational Modeling Environment (GNOME) was used (GNOME, 2019). This program uses a modeling software that takes into account recorded tides, currents, wind speeds and direction to estimate how a spill may travel in the environment. Currently this program is largely used for oil spills, but NOAA has a built-in option for general non-weathering chemical release. While this model isn't specific to hexavalent chromium, it is a reliable source of information on how a release may be transported in the Cooper River. The GNOME model was then compared to the risk model to validate the assumptions made.

In this risk assessment the average width (W), depth (Z or H), and streamflow (Q) from the previous section are used to calculate average stream velocity (u). This can be seen in which is essential to any fate and transport model.

$$U = \frac{Q}{ZW} \qquad \text{(IV-1)}$$

As flow varied with time the average stream velocity changed along with it; while the average width and depth of the river was assumed to remain constant. For example, if at

time (t) = 1hr the flow (Q) was 20,000 ft^3/s (560 m^3/s) and the width and depth were the same as mentioned above, average stream velocity (u) would be (560/(7.62 * 267m)) = 0.28. m/s. At t = 2 hr if the flow was now 57,300 ft^3/s (1604.4 m^3/s), then velocity would be 0.78 m/s.

4.2.1 Transport Concentration Equations

There are several transport equations for quantifying concentration after a contaminant release depending upon multiple variables that may or may not need to be included (for a list of possible transport equations the reader should refer to Quantitative Environmental Risk Analysis for Human Health by Fjeld et al., 2007). For this assessment both constant and instantaneous step equations were chosen to model the contaminant concentration.

Constant transport is chosen when an emission source continuously releases a set amount of emissions over a period of time with little to no fluctuation (Fjeld, Eisenberg, & Compton, 2007). For this assessment a constant transport was calculated under the assumption that each facility continuously released their reported chromium emissions throughout a year. This assumption would lead to a lower overall concentration downstream in the water as the release is more spread out over time. Furthermore, in constant transport equations it is assumed dispersion does not play a significant part and can be neglected from the equation (Fjeld, Eisenberg, & Compton, 2007). This allows the equation to focus solely on advection and leads to a simplified formula for concentration at any point down or upriver of the release site as seen in below. Constant transport also

does not take into account a time variable since concentration in the water should theoretically be constant with respect to time as well. However, for this model the varying flow (Q) for each time step was divided into the emission rate (S_0) so that the constant concentration could be seen with respect to the changing flow of the river. In lower flow (smaller Q) the concentration would be higher than it would be when the flow is higher.

$$\text{Constant: } C(x) = \frac{S_0}{Q} e^{-\sum \alpha(\frac{x}{u})} \quad \text{(IV-2)}$$

Where:

C(x)	=	Concentration with respect to distance down river from release (mg/L)
S_0	=	Constant emission rate (kg/s or mg/s)
Q	=	average river flow rate of water body (m^3/s)
α	=	removal rates from degradation, decay, and settling (s^{-1})
x	=	distance from release site (m)
u	=	average river velocity of water body (m/s)

Furthermore, in , the $\sum \alpha(\frac{x}{u})$ represents the sum of degradation rate, decay rate, and settling rate which are each represented by α's. However, hexavalent chromium does not decay, is assumed to not significantly degrade, and has a negligible ($< 1.0 \times 10^{-15}$ $mg/L^{-1}s^{-1}$) amount of mass settling out even at suspended solids concentration of 1,000 mg/L. This lack of settling mass is due to hexavalent chromium's extremely low Kd partition coefficient (19 L/kg(s)) (Fjeld, Eisenberg, & Compton, 2007). Therefore, the

$e^{-\sum \alpha(\frac{x}{u})}$ term approaches 1 as α goes to zero. This leads to a steady state equation of $C(x) = \frac{S_0}{Q}$ for hexavalent chromium. Hexavalent chromium's affinity to stay dissociated and mobile also leads to the assumption in this study that concentration in the water (C_W or C_L) is equal to total concentration (C_{tot}). Going forward C_W and C_{tot} will be interchangeable.

Instantaneous transport equations assume a sudden, short-term release of contaminant to the environment. This would be the case if a facility only released their emissions once a month, quarterly, or if an accidental spill occurred. Such a case could happen if a facility had a certain level of storage for waste that is used until full capacity and then released or if the production process only requires intermittent releases. This risk assessment runs a model for monthly releasing using the instantaneous model. Here both advection and dispersion would be important as the concentration would change significantly throughout time and distance depending on the conditions met throughout the river during transport. For instantaneous emissions the mass of pollutant is assumed to be released as an even distribution across the body of water at t = 1 second. At the release site at an instantaneous point of release the concentration equation is also in its steady state form of $C = S_0/Q$. However, for calculating concentration at a certain distance from the site the instantaneous model must be used and can be seen in

.

$$C(x,t) = \frac{S}{WH\sqrt{4\pi E_x t}} e^{\left[-\frac{(x-ut)^2}{4E_x t}\right]} \quad \text{(IV-3)}$$

Where:

C(x,t) = Concentration with respect to distance from release and time since release
S = Emission rate at time of release (kg/m^3)
W = Average width of river (m)
H = Average depth of river (m)
E_x = Dispersion Coefficient (m^2/s)
t = Time since release (s)
x, U are previously defined in

Here the dispersion coefficient is included to account for differences in river velocity with respect to depth and turbulence within the water. The dispersion coefficient is further defined by .

$$E_x = 0.011\left(\frac{u^2 W^2}{u^{*2} H}\right) \quad \text{(IV-4)}$$

Where:

$$u^* = \sqrt{gHs} = \text{shear velocity } \left(\frac{m^2}{s}\right) \quad \text{(IV-5)}$$

and:

g = acceleration due to gravity (9.8 m^2/s)

s = average slope of river (m/m)

In order to find the time when maximum concentration is reached at the desired distance (x) from the release site is used where all variables are previously defined. Following this, t_{max} can be plugged into for *"t"* in order to find the maximum concentration at the desired point.

$$t_{max} = \frac{-E_x + \sqrt{(E_x)^2 + (u)^2(x)^2}}{(u)^2} \quad \text{(IV-6)}$$

Finally, in order to calculate eventual dose and risk from consuming fish, a concentration within fish value must be found. This value, known as $C_{f,}$ is found by using

.

$$C_f = B_f * C_w \quad \text{(IV-7)}$$

Where:

B_f = Bioaccumulation factor of desired contaminant in fish

C_w = Concentration in water (in this study also C_{tot})

The bioaccumulation factor in fish for hexavalent chromium is 200 L/kg of fish which is higher than most other metals.

4.2.2 Dose Equations

To calculate dose (D), methods of contaminant uptake by humans or animals must be chosen. As mentioned, uptake via drinking water and consumption of river fish were selected as the two primary methods of exposure. The hexavalent chromium sites of interest are within close proximity to the most significant drinking water intake site for the Charleston metropolitan area (CWS, 2020) and in a popular fishing area (Burleson, 2020).

To calculate daily intake dose (mg/kgday) in drinking water five variables are required for the equation. These include uptake rate [CR (L/day)], body weight [BW (kg)], average lifetime [t_{avg} (years)], time exposed [t_e (years)], and the concentration in water [C (mg/L)] found in the transport equation. Similarly, for fish consumption daily dose a concentration in fish [C_f (mg/kg)] needs to be determined and the uptake rate is in grams/day.

Uptake rate for drinking water was assumed to be 1.5 L/day while uptake rate for fish consumption of recreational freshwater fish was assumed to be 8 g/day (Fjeld, Eisenberg, & Compton, 2007). Average body weight was chosen as 71.8 kg. Average lifetime (t_{ave}) was assumed to be 75 years. The dose calculation for consuming fish assumes an exposure time (t_e) of 70 years, assuming babies and young children would not consume high levels of fish. Meanwhile, for the drinking water dose calculation an exposure time of 75 years was assumed and thus equal to average lifetime. For drinking water dose expressions, although included in the equation, time exposed and average

lifetime actually cancel out because of this assumption. The daily dose equation for drinking water can be seen in while the dose calculation for consuming fish is .

$$D_w = \frac{CRC_w t_e}{BWt_{ave}} \quad \text{(IV-8)}$$

$$D_f = \frac{CRC_f t_e}{BWt_{ave}} \quad \text{(IV-9)}$$

4.2.3 Risk Equations

Once dose is found risk can then be calculated either stochastically or deterministically (Fjeld, Eisenberg, & Compton, 2007). Stochastic risk typically refers to a cancer-causing ability. This risk is related to an increased probability of getting cancer as the individual is exposed to higher doses of contaminant. Deterministic risk refers to harm that increases in severity with increasing dose. A chemical burn that is worse from a 1 molar acid solution than a 0.5 molar solution would be an example of deterministic risk. As discussed in the Background section, hexavalent chromium is a contaminant that has both deterministic and stochastic effects. This report mainly focuses on stochastic risk created by the hexavalent chromium pollution studied, but an overview of how to quantify both is provided below for clarity.

Deterministic risk is calculated by what is known as a Hazard Quotient (HQ). The HQ value is determined by .

$$HQ = \frac{D}{RfD} \quad \text{(IV-10)}$$

Where:

D = Calculated daily dose (mg/kgday)

RfD = Reference dose (accepted daily intake dose defined by the EPA)

A contaminant is likely to cause deterministic harm if the calculated Hazard Quotient is above 1. This makes sense as a value greater than 1 would require a daily intake dose higher than the acceptable reference level determined by the EPA. If the value is greater than 1 this does not mean there will be definite deterministic harm; rather it points to a need for concern at the possibility of harm.

In order to calculate stochastic risk, a value known as the cancer slope factor ($[mg/kgday]^{-1}$) must be obtained for the specific chemical. This is a variable that cancels out units with the daily dose rate and yields a unitless risk value. Currently, research on chromium's ability to cause cancer from inhalation is much more advanced than research on chromium's carcinogenic ability via ingestion. Therefore, the EPA has only published an official inhalation cancer slope factor for hexavalent chromium to date. However, in 2010 the EPA reported with a high level of confidence for an oral slope factor of 0.5 $(mg/kgday)^{-1}$ (Stern, 2010). This value was never officially published by the EPA, but it

received significant support from independent reviewers. Therefore, this value was chosen to be used for the stochastic risk calculations in this assessment. The stochastic risk calculation is seen in .

$$R = pD \qquad \text{(IV-11)}$$

Where:

p = Oral cancer slope factor

D = Daily dose (mg/kgday)

Regulators in the United States strive for risk values below 1.0×10^{-06} (1 in 1,000,000 affected) and anything above this is cause for concern for the EPA (Fjeld, Eisenberg, & Compton, 2007). However, the 0.02 ppb Public Health Goal for Hexavalent chromium in drinking water actually yields a risk of 2.0×10^{-07} which is even lower than the normal EPA guideline. Both risk values are used as guidelines for analyzing and understanding the results from this assessment provided in the following section.

4.3 Results and Discussion

In this section many data values presented in tables, graphs, and maps are the maximum possible concentration, dose, and risk calculated. This conservative approach is desired when performing risk calculations so that the audience fully understands the possible outcomes from the most extreme circumstances.

The results provided similar values for the risk from consuming fish and the risk from drinking contaminated water. This is purely due to the mathematical coincidence in the product values due to the variables used in each scenario. For example, in the fish dose calculation the numerators had to be multiplied by 10^{-3} because the uptake rate was in grams/day and the numerator needed to be in kg/day to cancel with bodyweight. One would think this would make the fish dose roughly 10^{-3} smaller than the water dose because water uptake rate is in L/day and doesn't need to be converted to cancel. However, the fish bioaccumulation factor for Cr (VI) is 2.0×10^{2} L/kg which effectively brought the fish dose and risk values to the same power as the water. The Fish and Water concentration, dose, and risk values will be discussed in their respective sections ahead.

4.3.1 Constant Release- Concentration, Dose, Risk

Constant release concentration is based largely on the flow rate of the water body as mentioned in 4.2.1. As a result, the constant release concentrations varied greatly dependent upon the flow chosen. The constant release the emission rates the release sites was simply calculated by converting the average releases from kg/year to mg/s. The emission rate for Nucor Steel was 2.2 mg/s while the emission rate for BP Chemical was

3.2 mg/s. For the majority of flows within the USGS data set the concentration was at most 4.23 x 10^{-06} mg/L for each respective release site. This value would be seen as negligible in drinking water because it only yields a maximum risk of 4.0 x 10^{-08}. However, at low flows the concentration, dose, and risk became notably worse as expected. At the time of flow direction reversal (<1 m^3/s) the concentration at the release site went as high as 0.08mg/L (80 ppb) at the Nucor Site and 0.11 mg/L (110 ppb) at the BP site. These low flow water concentrations led to significant doses and risks as seen in Figure IV-7. The concentration in fish at this time was also quite high at 23 mg/kg at the BP site and 16 mg/kg at the Nucor site.

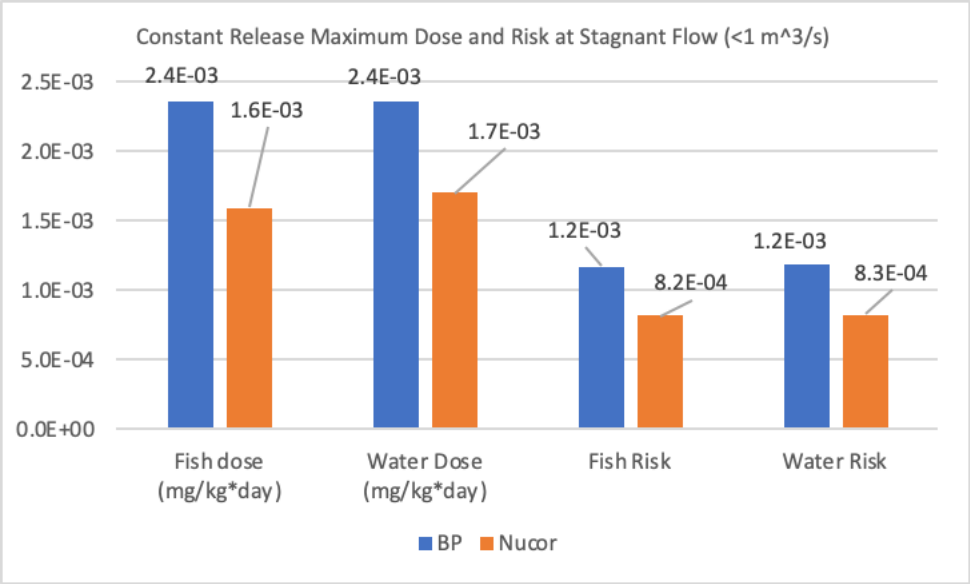


Figure IV-7: Maximum Doses and Risks for Constant Release.

(Release sites at time of flow direction reversal)

The high-risk value for consuming drinking water seen here is unlikely to actually cause harm to humans. The risk for drinking water contamination would only occur by transport upriver into the Durham Canal or flooding into the reservoir. The scenario discussed here relies on proximity to the release site and stagnant flow of water. In order to reach the canal, the contaminant would need to be transferred a significant distance and thus diluted by high flow. Similarly, in a flood scenario high flow would likely negate the high concentrations observed near the release sites.

The likelihood of a person catching a fish next to the release site during stagnant flow is also minimal. Yet, these values are still significant and require consideration in regard to fish. Although stagnant flow is minimal throughout a day, the Cooper River changes direction roughly every 5 hours and so a short period of low flow would happen multiple times throughout one day. Over time there is a strong possibility that fish would be present at the release site when the flow does become stagnant. This would greatly increase the concentration of hexavalent chromium the fish would be exposed to. A short period of exposure for a fish could lead to significant bioaccumulation. This scenario could lead to severe contamination in several fish, especially if they repeatedly travel through the release areas in a day. A fisherman could then catch these fish that may be currently in clean waters but had previously been contaminated. Consumption of fish could become harmful over time and possibly lead to the development of cancer. Figure IV-7 shows consumption of these fish could yield a significant risk to human health over time. The maximum risk value of 1.2×10^{-3} is over 1,000 times higher than the EPA's desired risk threshold of 1.0×10^{-06}.

The risk with constant release is largely focused around exposure directly at the release site. Concentrations away from the release site are likely negligible in most areas as the emissions get diluted with flow. It is crucial to recognize the possible effects on fish and therefore humans from contamination near release sites. The bioaccumulation of hexavalent chromium in fish makes this contaminant carry a high risk to fisherman regardless of where the fish are caught in the river or even the ocean. Fish in the Cooper River are a mixture of freshwater, saltwater, and diadromous which leads to a wide area these fish can travel throughout their lifetimes. A marine fish can become contaminated during high tide and then swim back to sea and be caught by a marine fisherman. The fishermen could still be catching contaminated fish even though the catch is nowhere near the chromium site.

4.3.2 Instantaneous Release- Concentrations

Instantaneous releases provide a different range of concerns than constant releases. Instantaneous releases normally contain a much larger mass of contaminant released in a smaller window of time. This characteristic leads to contaminant plumes that are largely uneven in concentration with respect to time and distance but carry substantially higher concentrations within the plume. This instantaneous release model was based on the assumption of monthly releases (thus 12 a year) as opposed to the previous continuous release model. In considering releases occurring only once a month the emission rates from both sites became much larger. The Nucor Steel site would now release roughly 5.83 kg each month. The emission rate became 5.83 kg/s because instantaneous release models assume a sudden release at time (t) = 1 second. Likewise,

the BP Chemical site now had an emission rate of 8.33 kg/s. This instantaneous model also assumed an even spread of concentration horizontally across the water body. The model focused on finding maximum concentrations at certain distances up and downriver from the release sites as noted in 4.1.5.

Another aspect that requires more attention is the possibility of flooding discussed in 4.1.3. For instantaneous releases plume can stay close together and carry high concentrations of contaminant. If flooding occurred the plume would be diluted by increase water levels, but it could still carry significant amounts of pollutant into flooded areas including the reservoir. That is why instantaneous releases can often be more toxic and deadly than constant releases. Therefore, the instantaneous release results reviewed ahead show higher concentrations, doses, and risks at every distance along the river compared to constant release data. The levels of Cr (VI)in the CWS discussed in 4.1.1 could be drastically increased by intense flood contamination. In this way, instantaneous releases should be looked at with increased concern.

Concentration versus distance time data can be seen in Figure IV-8, Figure IV-9, Figure IV-10, and Figure IV-11 below. Plots are for both sites and flow in each direction. Concentrations at certain distances are plotted by their respective colored lines. For each model the concentration can be seen to peak twice for the distances closer to the release site whereas the distances further away have steadier maximum concentrations for longer periods of time. The two peaks in the nearer locations (1, 1.75, or 2 miles) are due to the plume crossing the test area as flow increases and passes by and then again as flow decreases and begins to reverse. The concentration plateaus for the further sites (5, 5.25,

7 miles) show the plume having a stationary affect as it just reaches the sites before the tide reverse down-stream. Tide reversal downstream results in a delayed flow movement upstream and keeps the plume at the max concentration at the further locations for an extended period of time. Max flow occurs at half the time period for each model as flow is modeled from zero up to peak flow and back down to zero based on real time USGS data (StreamflowUSGS, 2019). The farthest distance (11 or 14.5 miles) are barely observed on the plots because the concentrations begin to decrease drastically after mile 7. Concentrations at 11 miles and further are at most 4.2×10^{-07} ppb and therefore not directly significant. This means concentrations reaching the Durham Canal (11 miles upriver of Nucor) intake on a regular basis are minute but this data still shows the possibility of hexavalent chromium reaching the canal in a normal tidal sequence.

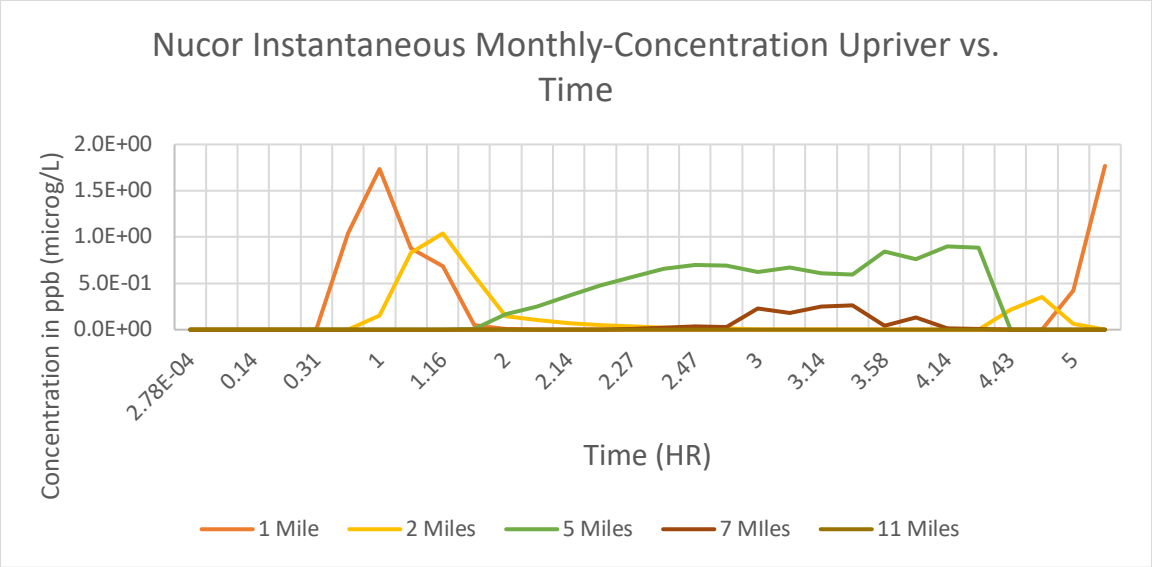


Figure IV-8: Nucor Instantaneous Release Upriver

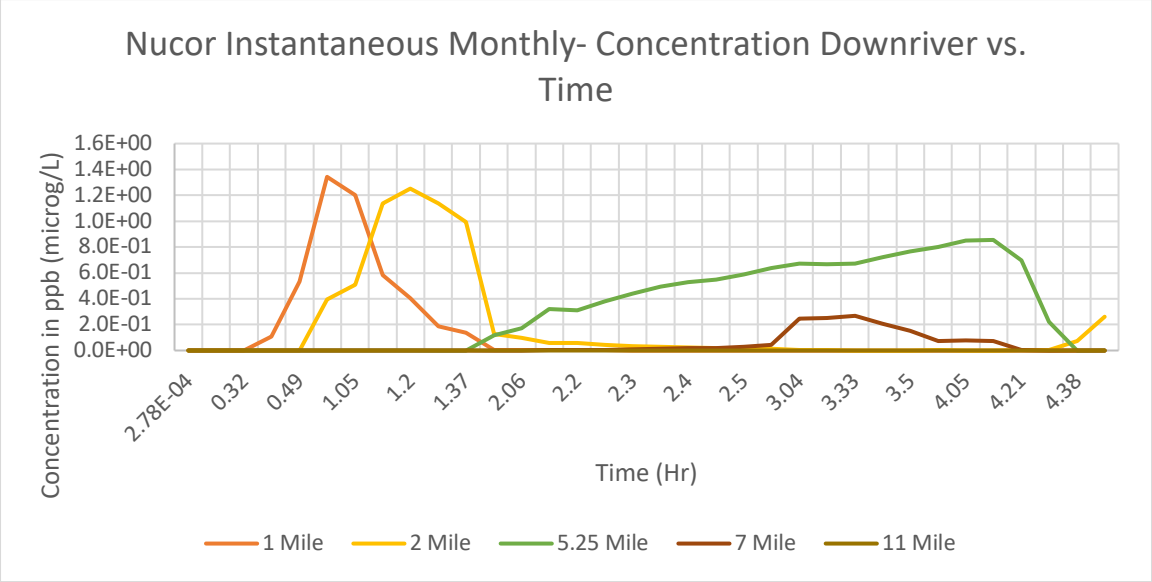


Figure IV-9: Nucor Instantaneous Release Downriver

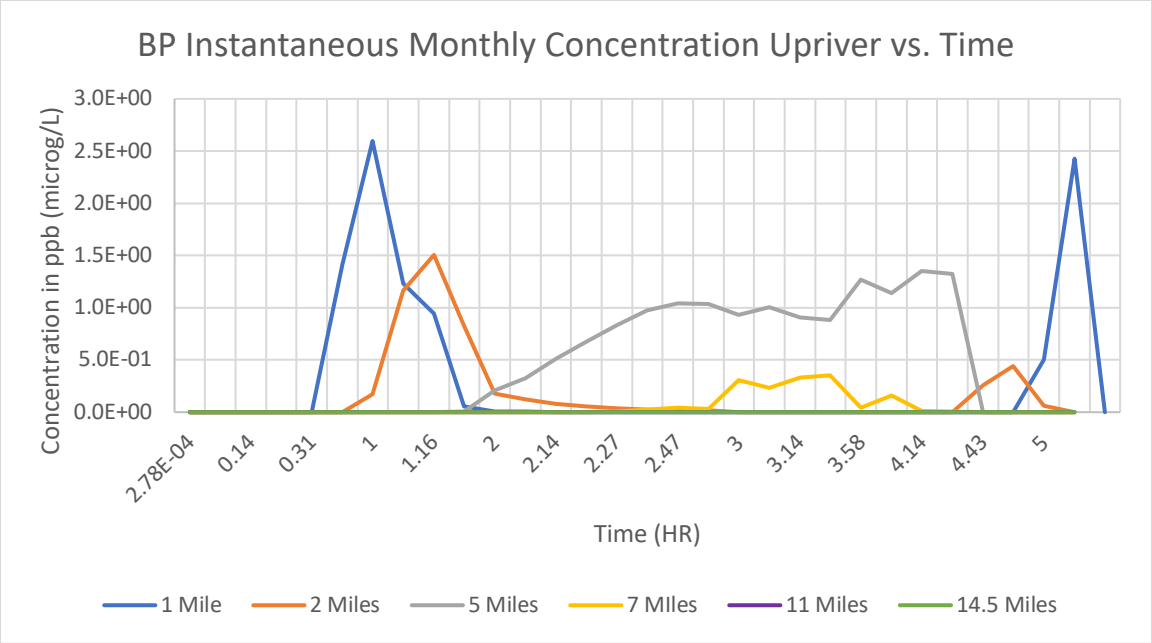


Figure IV-10: BP Instantaneous Release Upriver

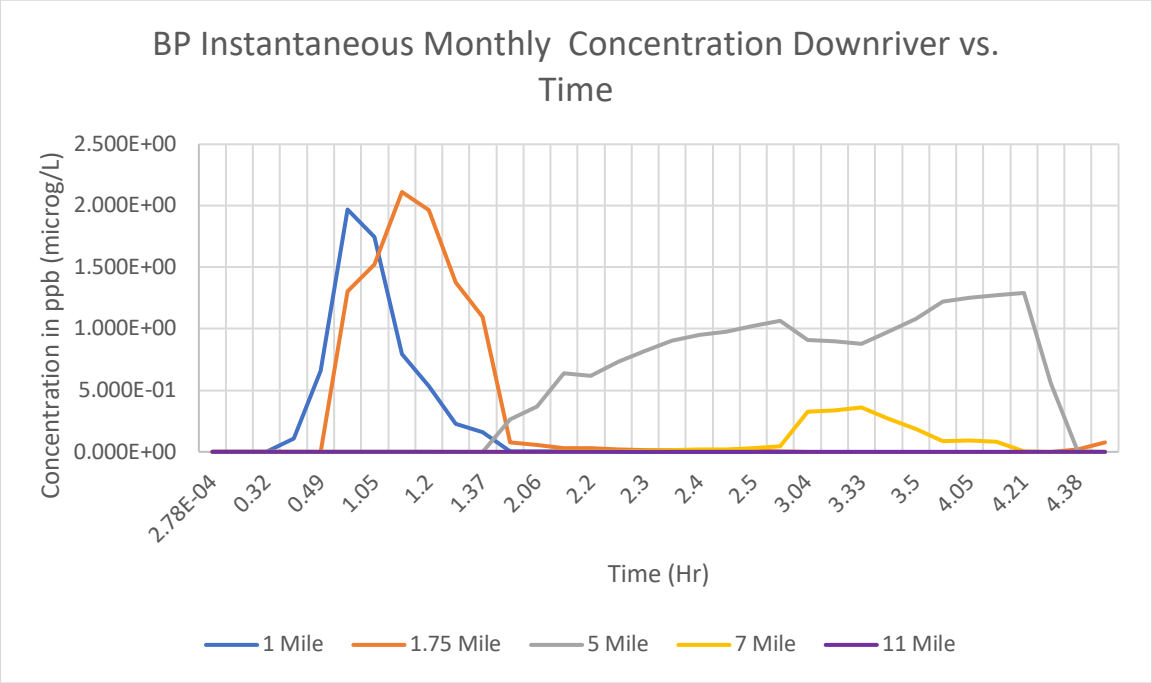


Figure IV-11: BP Instantaneous Release Downriver

Many of the concentrations on the figures above are significantly higher than the Public Health Goal set by the California EPA of 0.02 ppb. In fact, this value of 2.0×10^{-02} is not even visible on any of these concentrations graphs because it is 10 to 100 times smaller than the majority of the concentrations graphed. These values are not concentrations directly present within the drinking water reservoir; however, their presence in close proximity to the reservoir in a flood-prone area is a cause for concern.

Maps that show the maximum concentrations possible at various sites along the river were created in ArcGIS using TRI data and FEMA flood maps. The first map is for releases from Nucor (Figure IV-12) while the second is for BP (Figure IV-13). Max concentrations in the Cooper River can be seen color-coded in the legend (microg/L, ppb) while high risk flood zones are shaded in purple. The maps were made separately for each release because the assumptions with respect to time in this instantaneous model made it unlikely that instant releases from each site would happen at the same exact time to cause additions in concentrations and risk. Even modeled as individual events these maps clearly show the danger involving the proximity of contaminated water to drinking water.

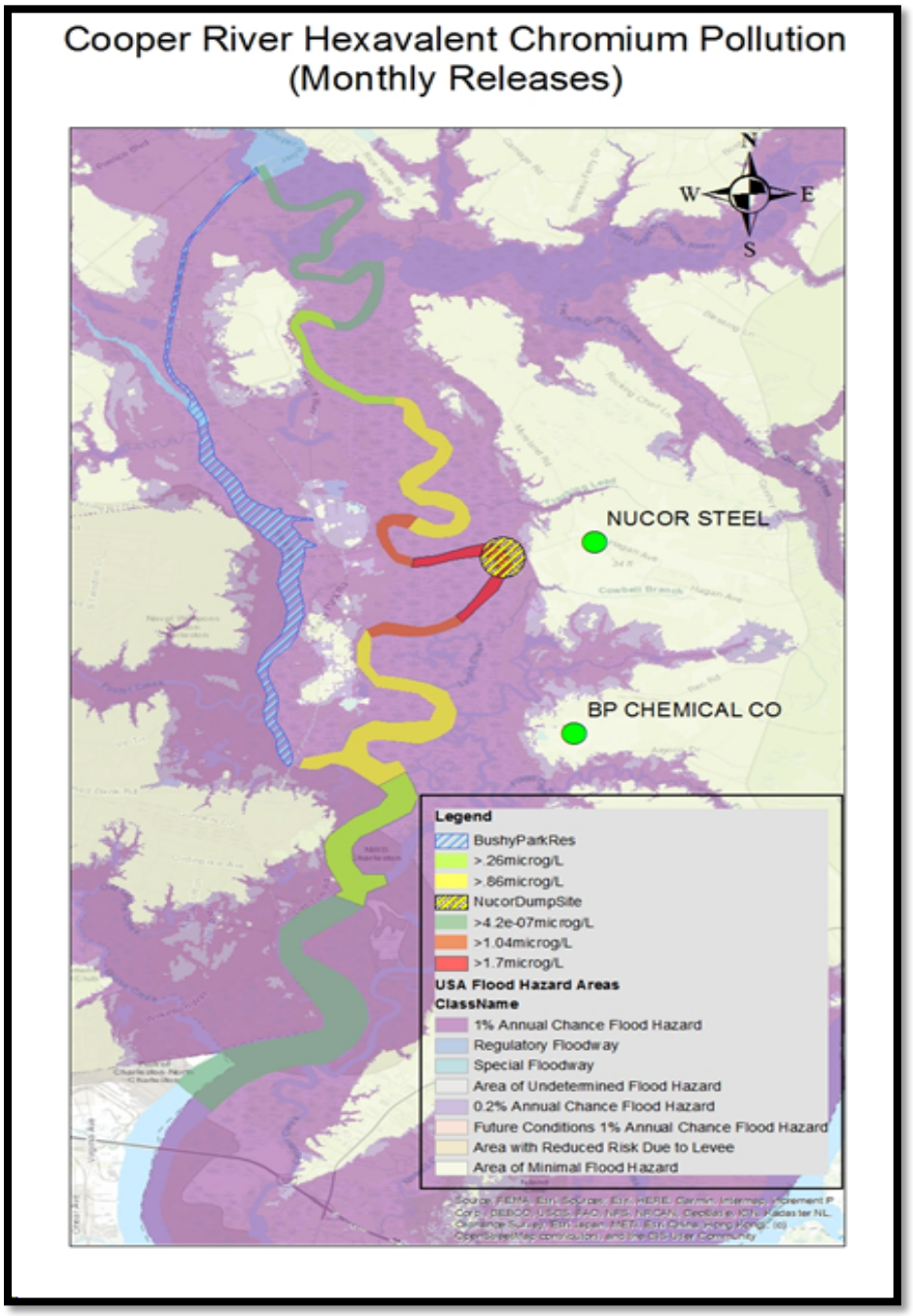


Figure IV-12: Map-Nucor Water Max Concentrations

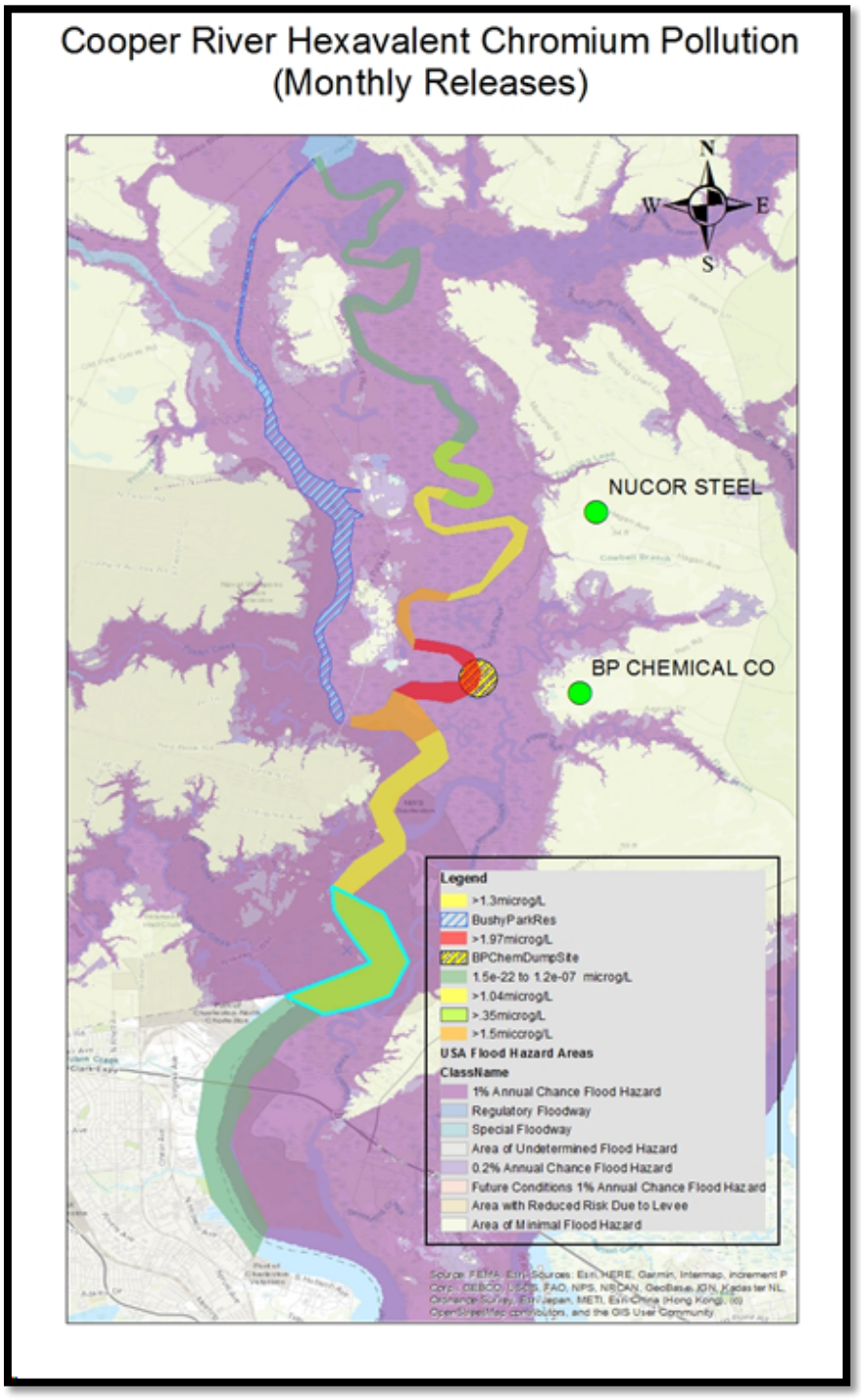


Figure IV-13: Map- BP Water Max Concentration

The maximum possible concentrations in fish were calculated from this water concentration data and can be seen in Table IV-1. Nucor with an instantaneous emission rate of 5.83kg/s had fish concentrations as high as 0.17 mg/kg up to 5.25 miles up or downriver. The levels stayed as high as 0.25 mg/kg at roughly the same distance from the BP site with an emission rate of 8.33 kg/s. Within 1 mile of Nucor, fish concentrations could be seen as high as 0.35 mg/kg. At the same distance for BP concentrations were as high as 0.52 mg/kg. Directly at the release site concentrations were calculated to be significantly higher regardless of flow because of the instantaneous assumption of immediate release (t = 1 s) and the steady state equation used for the release site. These concentrations at the release site averaged 1,226 mg/kg at Nucor and 1751 mg/kg at BP throughout various flows. Concentrations of this level would cause detrimental acute effects in fish and could even lead to fish kill off directly below the site (Aslam & Yousafzai, 2017). In reality, concentrations of this magnitude from an instantaneous release would only last for a small amount of time. For this reason, concentrations for most fish in the river would likely reflect the concentrations in downstream measurements that include dispersion, distance, and time. These fish concentrations can be seen mapped in Figure IV-14 and Figure IV-15.

Nucor Steel		BP Chemical	
Distance from Release (Miles)	Fish Concentration (mg/kg)	Distance from Release (Miles)	Fish Concentration (mg/kg)
Release site	1,226	Release site	1,751
1	0.27-0.35	1	0.39-0.52
2	0.21-0.25	1.75-2	0.30-0.42
5-5.25	0.17-0.18	5	0.25-0.27
7	5.0E-02	7	0.07
11	8.3E-08 - 8.7E-08	11-14.5	2.5E-08 - 2.9E-20

Table IV-1: Concentration in Fish

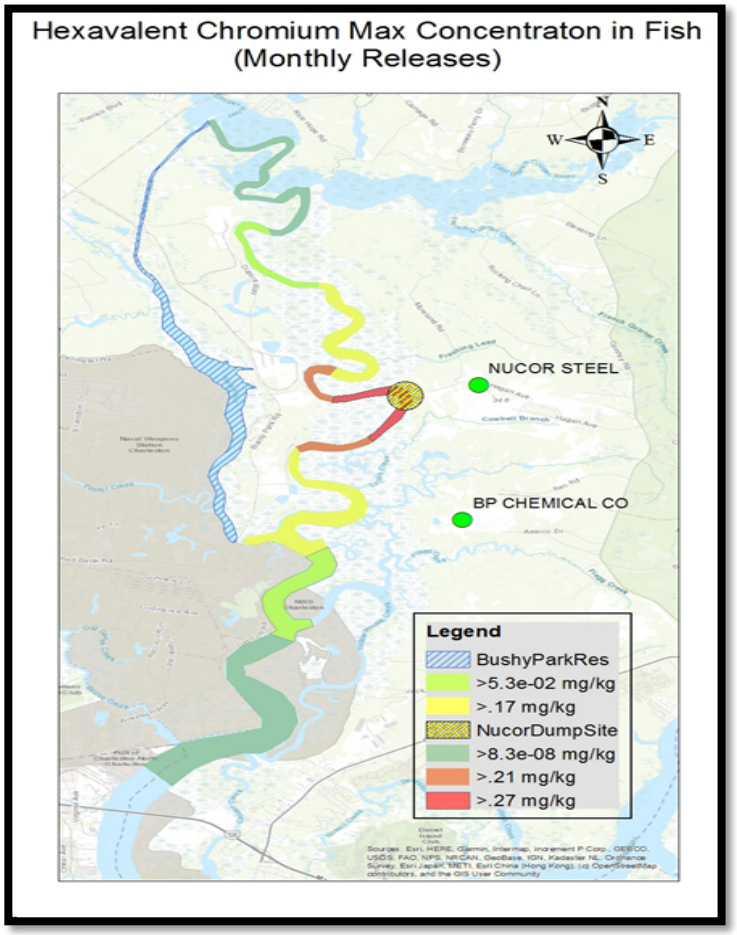


Figure IV-14: Map-Nucor Fish Max Concentrations

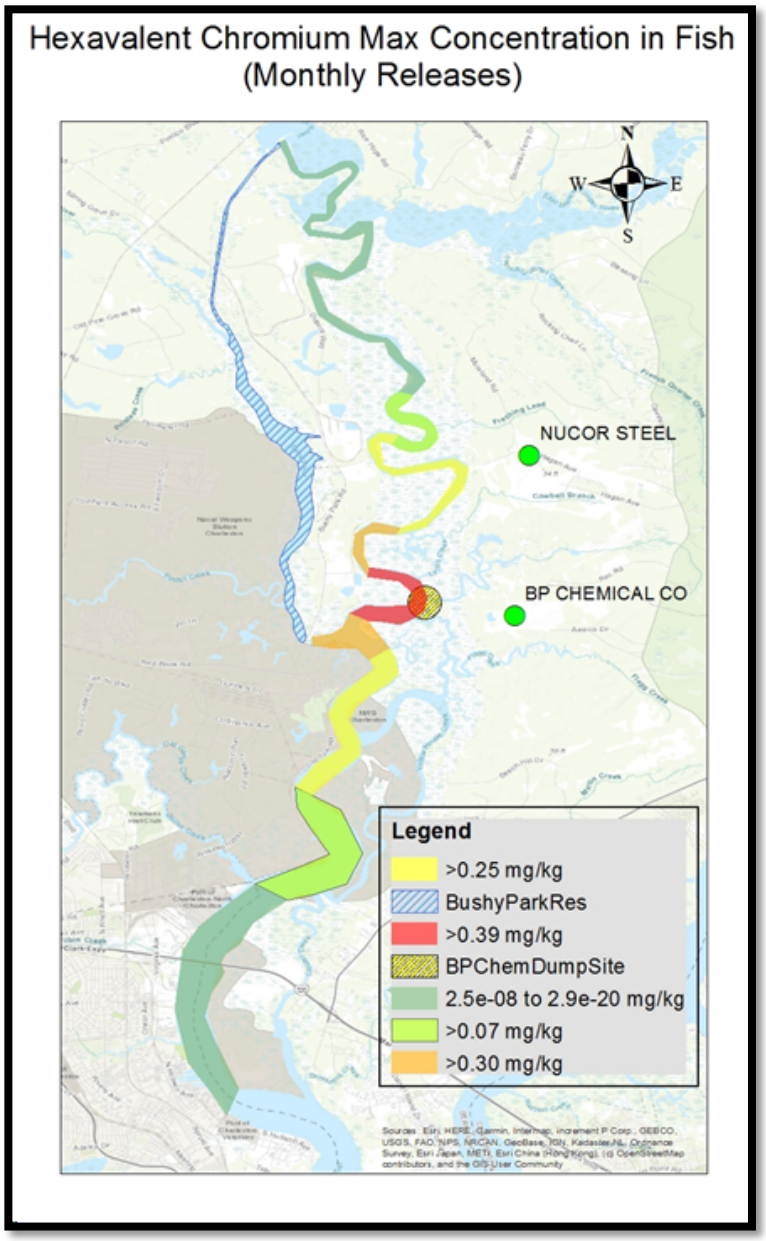


Figure IV-15: Map- BP Fish Max Concentrations

4.3.3 Instantaneous Risk

The concentration data above was input into the daily dose calculations mentioned in Dose Equations. Once dose values were calculated for consumption of fish and contaminated water, these daily doses were placed into the R = *p*D equation for stochastic risk.

Drinking water risk were as high as 1.8×10^{-05} for Nucor releases and 2.7×10^{-05} for BP releases within 1 mile of the sites. At 7 miles from the sites risk values were still higher than both the California Public Health Goal risk of 2.0×10^{-07} and the EPA's normal limit for human health risk of 1.0×10^{-06}. Risk values within 2 miles of the Nucor site were up to 12 times higher than the EPA risk limit and 60 times higher than the Public Health Goal risk. Likewise, concentrations within 2 miles of BP were 21 times higher than the EPA risk limit and 105 times larger than the PHG risk. These values display the possible impacts of the contaminant plume moving through different area of the Cooper River. Flooding at any location along these distances could compromise the reservoir's water quality. Risk values at release sites were significantly larger as expected and discussed in Instantaneous Release- Concentrations. Again, these values are possible at the time of release but are expected dissipate rather quickly. It is not likely these levels of risk could infiltrate the reservoir. However, if direct releasing did occur during a near-future flood scenario high concentrations of Cr (VI) could be carried from the release site directly into the reservoir. Mapped risk values can be seen in Figure IV-16 and Figure IV-17.

Nucor		BP	
Distance	RiskAtDistances	Distance	RiskAtDistances
Release site	4.8E-02 – 7.6E-02	Release site	6.8E-02 – 0.14
1	1.3E-05 - 1.8E-05	1	1.9E-05 - 2.7E-05
2	1.1E-05 - 1.2E-05	1.75-2	1.6E-05 - 2.1E-05
5-5.25	8.3E-06 - 9.4E-06	5	1.3E-05 - 1.4E-05
7	2.6E-06 - 2.7E-06	7	3.5E-06 - 3.7E-06
11	4.3E-12 - 4.4E-12	11 [] 14.5	1.2E-12 [] 1.5E-24

Table IV-2: Water Risk Levels

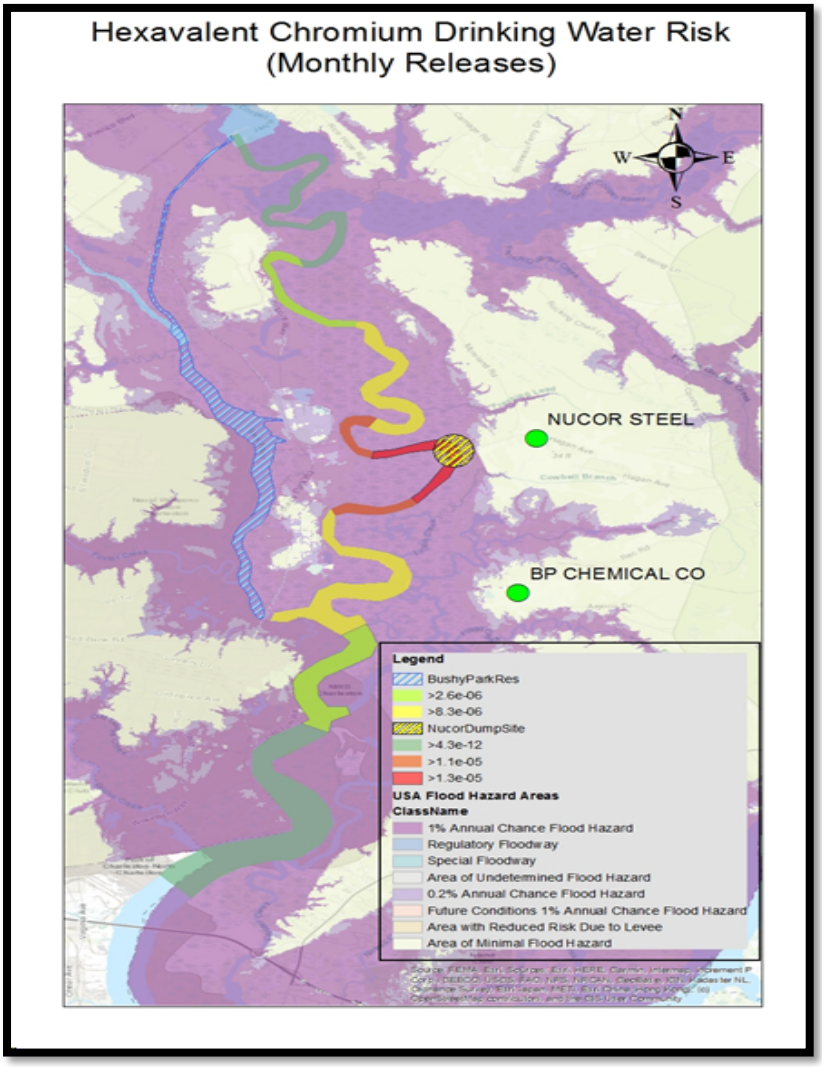


Figure IV-16: Map-Nucor Water Max Risk

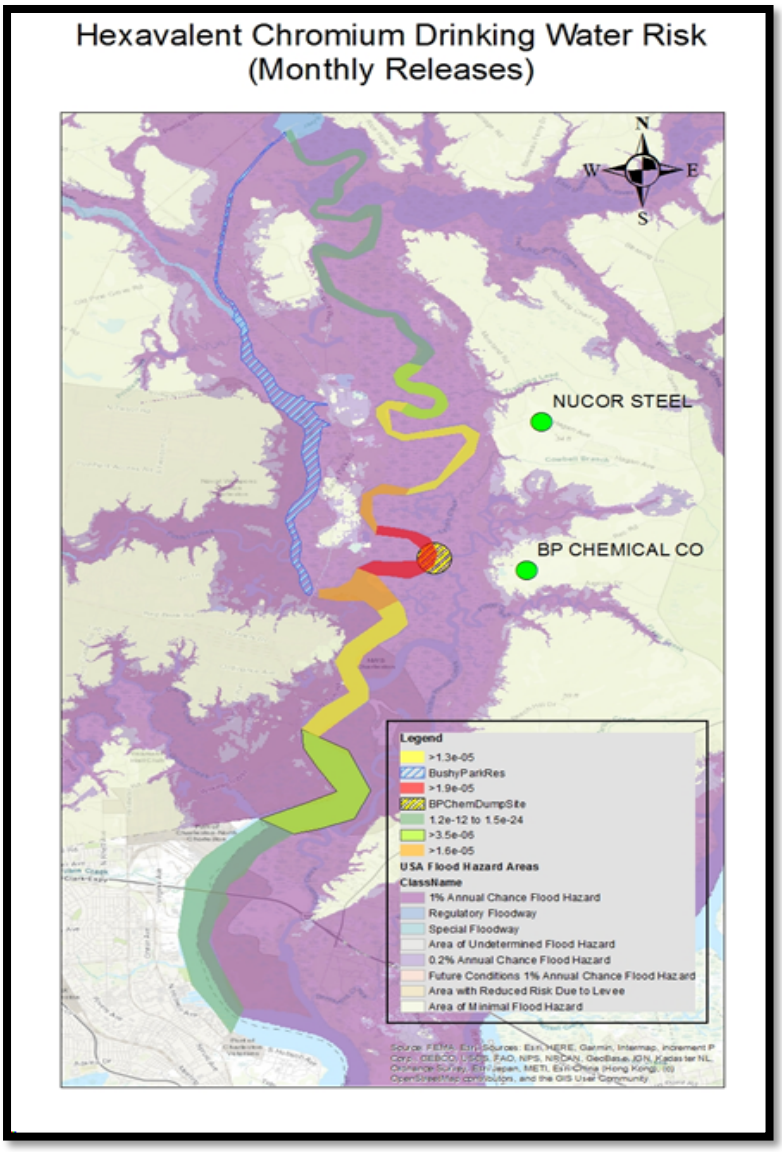


Figure IV-17: Map-BP Water Max Risk

Consumption of fish in the Cooper River provided similar risk values to drinking water risk. Risk values were above 10^{-05} within 2 miles and above 10^{-06} within 7 miles of each site as seen in Table IV-3. The fish risks were also significantly above both the federal EPA and California EPA's risk goals even at distances of 7 miles from release.

Nucor		BP	
Distance	RiskAtDistanceFish	Distance	RiskAtDistanceFish
Release site	4.7E-02 - 8.1E-02	Release site	6.6E-02 - .12
1	1.4E-05 - 1.8E-05	1	2.0E-05 - 2.7E-05
2	1.1E-05 - 1.3 E-05	1.75-2	1.6E-05 - 2.0E-05
5-5.25	8.9E-06 - 9.3E-06	5	1.3E-05 - 1.4E-05
7	2.7E-06 - 2.8E-06	7	3.7E-06 - 3.8E-06
11	4.3E-12 - 4.5E-12	11 [] 14.5	1.3E-12 [] 1.5E-24

Table IV-3: Fish Consumption Risk Levels

The difference to consider with fish risk is the bioaccumulation of contaminant over time leads to an increase in risk as releases continue. The original instantaneous models in this study were run with respect to one instant release of mass (5.83 kg for Nucor, 8.33 for BP). Realistically releases of this magnitude would be happening twelve times a year with the monthly release assumption. Therefore, it is highly likely that the same fish would be swimming through different contaminant plumes every month in this model. In order to understand how the risk of consuming fish would be affected as time progressed a risk model was calculated for a 5-year life span of a fish that encounters releases every month. This model was made to show how the risk increases over time if a fish is repeatedly exposed to contamination and then caught for consumption. As

expected, risk values increase as fish exposure continues to increase. Risk values of more than 10^{-04} reach out to 7 miles from release. Thus, even if a fish mostly lived 7 miles away from the release sites it could still accumulate substantial amounts of hexavalent chromium and become a high risk catch for a fisherman. Fish that are repeatedly contaminated within 2 miles of each site could lead to human health risks higher than 10^{-03}. These fish could harbor risk to fisherman over 1,000 times higher than what the EPA recommends and 10,000 times higher than what the California EPA's Public Health Goal. Consideration of repeated exposure is therefore necessary to understanding to overall risk posed for those that consume recreational fish. Values of 5-year risk can be seen below (Table IV-4).

Nucor		BP	
Distance	5YearRiskAtDistanceFish	Distance	5YearRiskAtDistanceFish
Release site	2.8 - 4.9	Release site	4.0 - 7.0
1	8.4E-04 - 1.10E-03	1	1.2E-03 - 1.6E-03
2	6.5E-04 - 7.8E-04	1.75-2	9.4E-04 - 2.6E-03
5-5.25	5.3E-04 - 5.6E-04	5	8.4E-03 - 1.6E-03
7	1.60E-04	7	2.2E-04 - 4.5E-04
11	2.6E-10 - 2.7E-10	11 [] 14.5	1.5E-10 [] 9.2E-23

Table IV-4: Risk of Repeated Contamination

Risk values for consuming fish that have been exposed to the contaminant plume only once are mapped in Figure IV-18 and Figure IV-19.

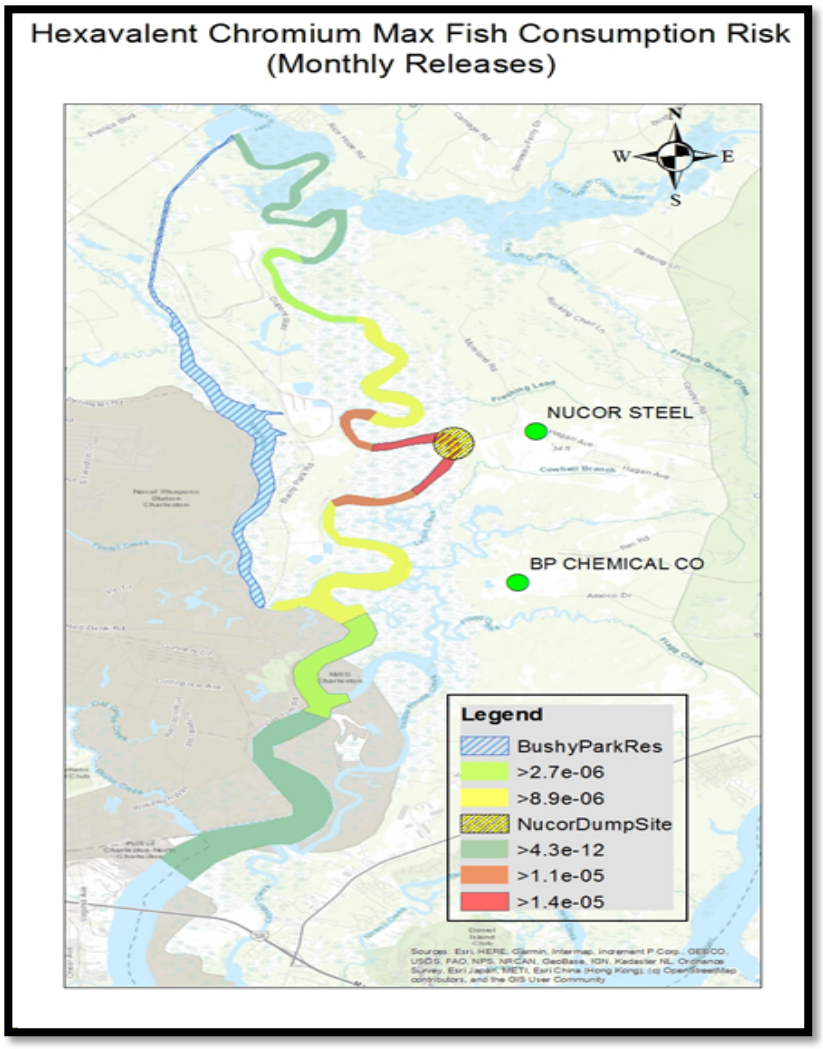


Figure IV-18: Map- Nucor Fish Max Risk

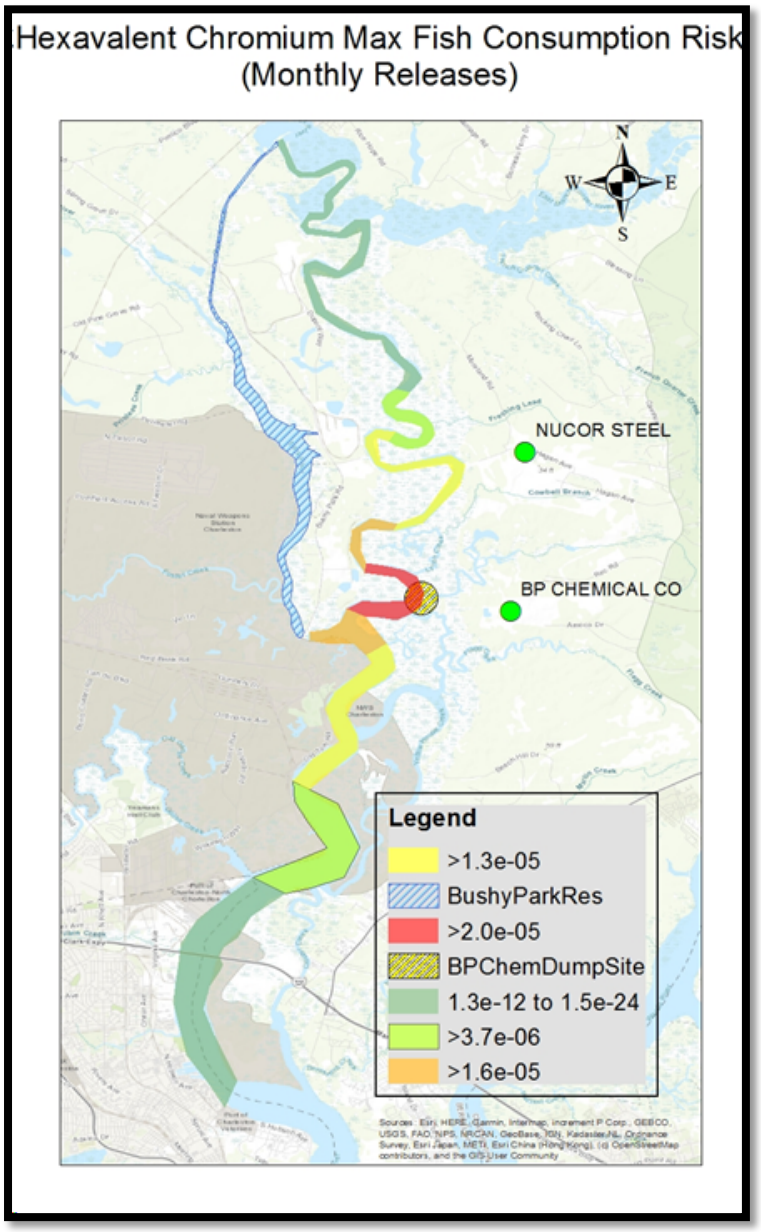


Figure IV-19: Map-BP Fish Max Risk

4.4 Possible Error

This study recognizes areas of possible error in calculations and assumptions. Models are created as imitations of natural events and rarely capture exact processes. Various assumptions were stated previously including the use of averages for dimensional measurements. A real river system would have varying widths, lengths, depths, and random objects within that would affect the concentration of a contaminant plume. Moreover, flow was measured using the best available USGS data, yet assumptions were made for these flows continuing throughout the system. In reality flows would vary across a river but average flow and velocity was assumed throughout.

Error could also be present from the chosen release sites for this assessment. For both Nucor and BP release sites were chosen along the Cooper River at spots that were closest to the facility locations. There may be a difference in where these facilities actually release Cr (VI) which could affect modeling data.

In modeling risk, it is hard to capture the true harm that can come from a contaminant release. Each organism is affected differently and even human to human effects can vary. This report strove to provide a general maximum possible risk for the release data used and for the models built.

4.5 Risk Assessment-Future Work

In future research the use of advanced contaminant fate and transport modeling software would be beneficial in visualizing the risks that accompany releases and providing transparency for affected citizens. Much of this work was conducted by creating models with differential equations for fate and transport modeling learned while taking Environmental Risk Assessment at Clemson. There was minimal use of previously designed modeling interfaces unless necessary to gain a basic understanding of chemical transport (GNOME, 2019). Future work should focus on creating fate and transport modeling interfaces that can be used specific to a chemical's properties. There is a need for a graphical interface where citizens can go online, type in a chemical and a location of a spill and see where the plume may go. While creating this assessment it was difficult to find models that would be easy for the general public to use. Most chemical fate and transport models are expensive or require the knowledge of advanced coding. Transparency to the public should be of main concern moving forward.

An analysis of possible deposition of hexavalent chromium from air emissions onto the Bushy Park reservoir would be a useful study. Nucor and BP, along with a few electric power plants in close proximity, release chromium air emissions as well and it would be interesting to calculate possible deposition on the reservoir. These air emissions may be another route for hexavalent chromium to enter the drinking water system.

Furthermore, it is suggested that field studies of fish in the Cooper River be conducted to test for traces of hexavalent chromium. Fishing regulations should also be reevaluated based on emissions from the EPA's TRI data. Beneficial work could come

from analyzing TRI emissions data for toxic and carcinogenic pollutants and researching proximities to major fishing areas throughout the state.

Finally, water treatment facilities are encouraged to increase awareness about the hexavalent chromium problem that is infiltrating the nation's drinking water supply. It is suggested that regular testing for hexavalent chromium be implemented throughout the country. This report hopes the EPA will work diligently to finish their reevaluation of hexavalent chromium's health effects through ingestion and create a new Maximum Contaminant Level that protects human health.

V. CONCLUSION

Continued use of hexavalent chromium in various industries has led to severe contamination throughout the United States and has compromised the drinking water of hundreds of millions of Americans. The persistent health effects of Cr (VI) have led to extensive research regarding alternatives to chromium in industrial processes over the past two decades. One of the main industries of focus has been metal manufacturing because of the significant use of chromium to create anti-corrosion oxide layers to protect various metals. A possible alternative that has continued to gain support is titanium-based oxides (titanate) because of their strong anti-corrosive ability and biological compatibility. The first objective of the research herein was to compare the environmental impacts of a hexavalent chromium-based oxide coating against a titanium-based oxide coating to better understand the effect on emissions if industry moved towards titanium-based coatings. A life cycle assessment (LCA) was conducted to successfully accomplish this goal. The results of the LCA showed lower environmental impacts for the titanium-based process in nine out of ten impact categories. Most importantly, titanium showed substantially lower impacts in the three main categories of concern: human health cancer, human health non-cancer harm, and ecotoxicity. These findings provide further support for a shift away from chromium-based processes and toward titanium-based processes in the metal manufacturing sector.

Secondly, a risk assessment was conducted to quantify the possible risk to human health from Cr (VI) releases at two major emissions sites within South Carolina. The sites

of interest had the most significant emissions of hexavalent chromium waste directly to freshwater in the state. The area of focus was along the Cooper River, a major fishing and industrial river north of Charleston, S.C. The sites were located within 3 miles of the largest drinking water source for the Charleston Metropolitan area, the Bushy Park Reservoir. The observed area was also found to be in a FEMA high risk flood zone which could lead to a contamination breach in a flood scenario.

Contaminant releases were modelled both as constant and instantaneous emissions. Concentrations were calculated as a function of distance from release site and time of release. Risk was calculated for humans via the ingestion of contaminated drinking water and consumption of fish. Results showed significant levels of bioaccumulation in fish that would warrant concern for consumption of fish in the river. Moreover, in the instantaneous model, the maximum water concentrations within 7 miles of the release sites were 10 times higher than the California EPA's public health goal (0.02 ppb) for drinking. Similarly, the concentrations were up to 130 times higher within 2 miles of the release sites. The drinking water of roughly 800,000 people could be contaminated if these Cr (VI) emissions infiltrated the reservoir in a flood scenario.

The ingestion of contaminated fish and drinking water in this study area could create concerning levels of risk that exceed the EPA risk threshold of 1.0×10^{-6}. Results showed risk levels above this threshold as far as 7 miles away from the release sites. Therefore, this assessment demonstrated the possibility of developing cancers from exposure to current Cr (VI) releases along the Cooper River.

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